(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 February 2017 (09.02.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/023777 A1

(51) International Patent Classification:
C07C 51/09 (2006.01) *C08G 63/08* (2006.01)
C07C 51/12 (2006.01) *C08G 63/82* (2006.01)
C07C 57/04 (2006.01)

(21) International Application Number:
PCT/US2016/044772

(22) International Filing Date:
29 July 2016 (29.07.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/199,918 31 July 2015 (31.07.2015) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: PRODUCTION SYSTEM/PRODUCTION PROCESS FOR ACRYLIC ACID AND PRECURSORS THEREOF

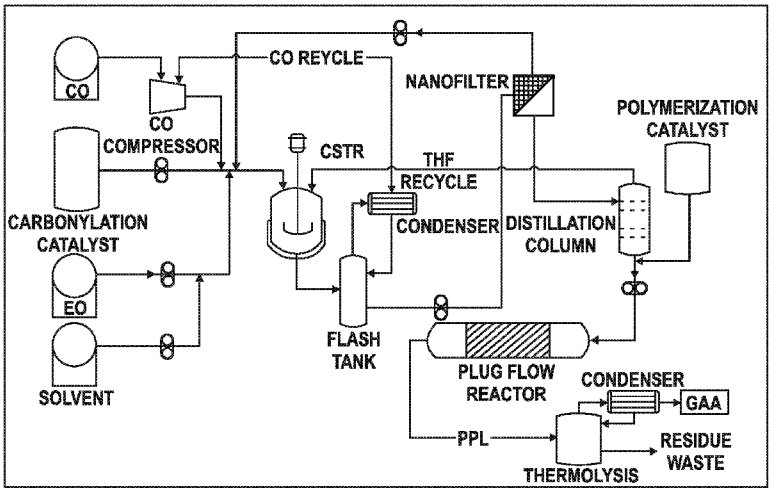


FIG. 1

(57) **Abstract**: Provided herein are systems, and methods of using such systems, for producing acrylic acid from ethylene oxide and carbon monoxide on an industrial scale. The production system/production processs has various unit operations, including, for example, a β-propiolactone production system/production process configured to produce β-propiolactone from ethylene oxide and carbon monoxide; a polypropiolactone production system/production process configured to produce polypropiolactone from ?-propiolactone; and a glacial acrylic acid production system/production process configured to produce acrylic acid with a high purity by thermolysis of polypropiolactone.

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PRODUCTION SYSTEM/PRODUCTION PROCESS FOR ACRYLIC ACID AND PRECURSORS THEREOF

FIELD

[0001] The present disclosure relates generally to systems and methods for producing acrylic acid and precursors thereof, including β-propiolactone and polypropiolactone, from ethylene oxide and carbon monoxide.

BACKGROUND

[0002] Polypropiolactone is a biodegradable polymer that can be used in many packaging and thermoplastic applications. Polypropiolactone is also a useful precursor for the production of acrylic acid. Polypropiolactone may serve as a precursor for glacial acrylic acid, which is in high demand for the production of polyacrylic acid-based superabsorbent polymers, detergent co-builders, dispersants, flocculants and thickeners. One advantage of polypropiolactone is that it can be safely transported and stored for extended periods of time without the safety or quality concerns associated with shipping and storing glacial acrylic acid. There additionally is interest in glacial acrylic acid which can be produced from biomass-derived feedstock, petroleum-derived feedstock, or combinations thereof. Given the size of the acrylic acid market and the importance of downstream applications of acrylic acid, there is a need for industrial systems and methods to produce acrylic acid and precursors thereof.

BRIEF SUMMARY OF THE INVENTION

[0003] Provided herein are systems and processes for the production of acrylic acid and precursors thereof, including β-propiolactone and polypropiolactone, and methods of using such production system/production processs. In some aspects, provided is a production system/production process and a production process for glacial acrylic acid from ethylene oxide and carbon monoxide that includes a β-propiolactone production system/production process, a carbonylation catalyst recycling apparatus, a β-propiolactone purification system, a

polypropiolactone production system/production process, and a glacial acrylic acid production system/production process.

[0004] In some embodiments, the β-propiolactone production system/production process includes a carbon monoxide source, an ethylene oxide source, a carbonylation catalyst source, a solvent source, and a carbonylation reactor. In certain variations, the carbonylation reactor has at least one inlet to receive carbon monoxide from the carbon monoxide source, ethylene oxide from the ethylene oxide source, carbonylation catalyst from the carbonylation catalyst source, and solvent from the solvent source; and an outlet to output a first β-propiolactone stream, wherein the first β-propiolactone stream comprises β-propiolactone, solvent, ethylene oxide, carbonylation catalyst, acetaldehyde, and succinic anhydride.

[0005] In some embodiments, the carbonylation catalyst recycling apparatus is configured to separate at least a portion of the catalyst from the first β-propiolactone stream and produce a recycle catalyst stream and a second β-propiolactone stream. In some variations, the recycle catalyst stream includes separated carbonylation catalyst. In some variations, the second β-propiolactone stream includes β-propiolactone, solvent, ethylene oxide, catalyst, acetaldehyde, and succinic anhydride. In other embodiments, the carbonylation catalyst recycling apparatus has an inlet to receive the first β-propiolactone stream from the β-propiolactone production system/production process; a recycle outlet to output the recycle catalyst stream to the carbonylation reactor; and a β-propiolactone outlet to output the second β-propiolactone stream.

[0006] In other embodiments, the β-propiolactone purification system includes an evaporator, a stripper, and a vacuum column. In some variations, the evaporator is configured to receive the second β-propiolactone stream from the carbonylation catalyst recycling apparatus, and separate the second β-propiolactone stream into:

a first overhead stream that includes (i) at least 75 wt% of solvent, (ii) less than 20 wt% of β-propiolactone, and (iii) less than 5 wt% of ethylene oxide and acetaldehyde, and

a first bottoms stream that includes: (i) at least 75 wt% of β-propiolactone, (ii) less than 20 wt% of solvent, and (iii) less than 5 wt% of catalyst, acetaldehyde, and succinic anhydride.

[0007] In some variations, the stripper is configured to receive the first overhead stream from the evaporator, and separate the first overhead stream into:

a second overhead stream that includes (i) at least 25 wt% of ethylene oxide and acetaldehyde, and (ii) less than 75 wt% of solvent,

a side stream comprising solvent, and

a second bottoms stream comprising β-propiolactone.

[0008] In some variations, the vacuum column is configured to receive the first bottoms stream from the evaporator, and the second bottoms stream from the stripper and mix the first bottoms stream and the second bottoms stream to produce a mixed bottoms stream, separate the first bottoms stream and second bottoms stream into: a third overhead stream comprising solvent, and a third bottoms stream comprising β-propiolactone.

[0009] In some embodiments, the polypropiolactone production system/production process includes:

a polymerization initiator or catalyst source;

at least one polymerization reactor to receive the third bottoms stream from the β-propiolactone purification system and the polymerization initiator or catalyst from the polymerization initiator or catalyst source, and to output a polypropiolactone stream, wherein the polypropiolactone stream comprises polypropiolactone and β-propiolactone.

[0010] In other embodiments, the glacial acrylic acid production system/production process includes a thermolysis reactor, which has an inlet to receive the polypropiolactone stream from the polypropiolactone production system/production process, and an outlet to

output a glacial acrylic acid stream, wherein the glacial acrylic acid stream comprises glacial acrylic acid.

[0011] In other aspects, provided is a polypropiolactone production system/production process that includes: a β-propiolactone source; a polymerization initiator or catalyst source; a first polymerization reactor; and a second polymerization reactor.

[0012] In some variations, the first polymerization reactor includes: a β-propiolactone inlet to receive β-propiolactone from the β-propiolactone source; a first catalyst inlet to receive catalyst from the polymerization catalyst source; and a first mixture outlet to output a first mixture. In one variation, the first mixture comprises polypropiolactone, β-propiolactone, and polymerization catalyst.

[0013] In other variations, the second polymerization reactor positioned after the first polymerization reactor, and includes: a mixture inlet to receive the first mixture from the first polymerization reactor; a second catalyst inlet to receive additional polymerization catalyst from the carbonylation catalyst source; and a second mixture outlet to output a second mixture. In one variation, the second mixture comprises polypropiolactone, β-propiolactone, and polymerization catalyst.

[0014] In certain aspects, provided is a β-propiolactone polymerizer that includes: a mixing zone configured to mix β-propiolactone and a catalyst; and a plurality of cooling zones positioned after the mixing zone. In some variations, the β-propiolactone polymerizer has a reaction length. In certain variations, up to 95% of the β-propiolactone is polymerized in the presence of the initiator or catalyst to form polypropiolactone in the first 25% of the reaction length.

[0015] In other aspects, provided is a method for continuously producing polypropiolactone, that includes:

continuously feeding β-propiolactone into a first reactor;

continuously feeding catalyst into the first reactor;

producing a first mixture comprising polypropiolactone, unreacted β-propiolactone, and residual catalyst in the first reactor,

transferring the first mixture from the first reactor to a second reactor;

feeding additional catalyst from the catalyst source to the second reactor;

producing a second mixture comprising polypropiolactone, unreacted β-propiolactone, and residual catalyst in the second reactor.

[0016] In some variations of the method, the first reactor has: a β-propiolactone inlet to receive the β-propiolactone from a β-propiolactone source; a first catalyst inlet to receive the catalyst from a catalyst source; and a first mixture outlet to output the first mixture. In other variations of the method, the second reactor has: a mixture inlet to receive the first mixture from the first reactor; a second catalyst inlet to receive the additional catalyst from the catalyst source; and a second mixture outlet to output the second mixture.

[0017] In yet other aspects, provided is a polypropiolactone production system/production process that includes: a β-propiolactone source; a first reactor; and a second reactor. In some embodiments, the first reactor has: a β-propiolactone inlet to receive β-propiolactone from the β-propiolactone source, a bed of supported catalyst or supported catalyst precursor, and a first mixture outlet to output a first mixture. In one variation, the first mixture comprises polypropiolactone and unreacted β-propiolactone. In other embodiments, the second reactor is positioned after the first reactor. In some variations, the mixture inlet is configured to receive the first mixture from the first reactor, a second bed of supported catalyst or supported catalyst precursor, and a second mixture outlet to output a second mixture. In one variation, the second mixture comprises polypropiolactone and unreacted β-propiolactone.

[0018] In yet other aspects, provided is a solid transportable polymer composition that includes: at least 95 wt% of β-propiolactone; less than 10 ppm of cobalt or ions thereof; less

than 10 ppm of aluminum or ions thereof; less than 10 ppm acetic acid; and less than 10 ppm of tetrahydrofuran.

[0019] In another aspect, provided is a β-propiolactone purification system that includes: an evaporator; a first column, and a second column. In some embodiments, the evaporator configured to receive a feed stream, wherein the feed stream comprises β-propiolactone, solvent, and separate the feed stream into: a first overhead stream comprising: (i) at least 75 wt% solvent, and (ii) at most 20 wt% β-propiolactone; and a first bottoms stream comprising: (i) at least 75 wt% β-propiolactone, and (ii) at most 20 wt% solvent.

[0020] In some variations, the first column is configured to receive the first overhead stream from the evaporator, and separate the first overhead stream into: a second overhead stream comprising: (i) at least 35 wt% ethylene oxide, and (ii) at most 60 wt% solvent; a side stream comprising solvent; and a second bottoms stream comprising at least 75 wt% β-propiolactone.

[0021] In other variations, the second column is configured to receive the first bottoms stream from the evaporator, and the second bottoms stream from the first column, and separate the first bottoms stream and second bottoms stream into: a third overhead stream comprising at least 95 wt% solvent; and a third bottoms stream comprising at least 95 wt% β-propiolactone.

[0022] In one aspect, provided is a β-propiolactone composition that includes at least 95 wt% of β-propiolactone; less than 10 ppm of cobalt or ions thereof; less than 10 ppm of aluminum or ions thereof; less than 10 ppm acetic acid; and less than 10 ppm of tetrahydrofuran.

[0023] In yet other aspects, provided is a β-propiolactone production system/production process that includes: a carbon monoxide source; an ethylene oxide source; a carbonylation catalyst source; a solvent source; a recycled solvent storage tank; a reactor; and a purification apparatus. In some embodiments, the reactor has: at least one inlet to receive carbon monoxide

from the carbon monoxide source, ethylene oxide from the ethylene oxide source, carbonylation catalyst from the carbonylation catalyst source, and solvent from the solvent source and the recycled solvent storage tank; and an outlet to output a mixture, wherein the mixture comprises β-propiolactone, solvent, unreacted carbon monoxide, unreacted ethylene oxide, and carbonylation catalyst. In other embodiments, the purification apparatus is configured to: separate solvent from the mixture, and transfer the separated solvent to the recycled solvent reservoir.

[0024] In one aspect, provided is a glacial acrylic acid production system/production process that includes: a polypropiolactone source; and a reactor. In some embodiments, the polypropiolactone source includes: at least 95 wt% of polypropiolactone; less than 10 ppm of cobalt or ions thereof; less than 10 ppm of aluminum or ions thereof; less than 10 ppm acetic acid; and less than 10 ppm of tetrahydrofuran. In other embodiments, the reactor has: an inlet configured to receive the polypropiolactone from the polypropiolactone source; and an outlet configured to output a mixture, wherein the mixture comprises glacial acrylic acid.

[0025] In yet other aspects, provided is a separation system that includes: a feed source; a membrane; a first pump; and a second pump. In some embodiments, the membrane has: an inlet to receive a feed stream from the feed source, wherein the feed stream comprises β-propiolactone, catalyst and solvent; a catalyst outlet to output a catalyst recycling stream comprising catalyst and solvent; and a β-propiolactone outlet to output a β-propiolactone stream comprising β-propiolactone and solvent. In other embodiments, the first pump is configured to pump the feed stream from the feed source to the membrane. In yet other embodiments, the second pump is configured to pump the catalyst recycling stream to a β-propiolactone production system/production process.

DESCRIPTION OF THE FIGURES

[0026] The present application can be best understood by reference to the following description taken in conjunction with the accompanying figures, in which like parts may be referred to by like numerals.

[0027] FIG. **1** is a schematic illustration of a system to produce acrylic acid from carbon monoxide and ethylene oxide.

[0028] FIG. **2** is a schematic illustration of the unit operations to produce polypropiolactone from β-propiolactone, and glacial acrylic acid from polypropiolactone.

[0029] FIG. **3** is a schematic illustration of a carbonylation catalyst recycle system that employs membranes, configured to isolate residual carbonylation catalyst from a β-propiolactone product stream.

[0030] FIG. **4A** is a schematic illustration of a system for converting β-propiolactone to polypropiolactone that involves the use of two continuous stirred-tank reactors in series.

[0031] FIG. **4B** is a schematic illustration of a system for converting β-propiolactone to polypropiolactone that involves the use of two loop reactors in series.

[0032] FIG. **5** is a schematic illustration of a system for converting β-propiolactone to polypropiolactone that involves a plug flow reactor with multiple cooling zones.

[0033] FIGS. **6-13** depict various configurations of production system/production processs to produce glacial acrylic acid from ethylene oxide and carbon monoxide, via the production of β-propiolactone and polypropiolactone.

[0034] FIG. **14** illustrates an embodiment of an acrylic acid production system/production process described herein.

[0035] FIG. **15** illustrates an embodiment of a carbonylation reaction system described herein.

[0036] FIG. **16** illustrates an embodiment of a BPL purification system described herein.

[0037] FIGS. **17-20** are plots associated with Example 1 and show a plot of PPL and bPL peak absorbances as a function of time; an ^{1}H NMR of the isolated solid; a TGA of the isolated solid; and Melt rheology data of the isolated solid at 120°C.

[0038] FIGS. **21-24** are plots associated with Example 2 and show a plot of PPL and bPL peak absorbances as a function of time; an ^{1}H NMR of the isolated solid; a TGA of the isolated solid; and Melt rheology data of the isolated solid at 120°C.

[0039] FIGS. **25-28** are plots associated with Example 4 and show ^{1}H NMR plots indicating recovery of acrylic acid .

[0040] FIGS. **29** are plots associated with Example 5 and shows an ^{1}H NMR plot indicating recovery of acrylic acid.

DETAILED DESCRIPTION

[0041] The following description sets forth exemplary methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

Definitions

[0042] Definitions of specific functional groups and chemical terms are described in more detail below. The chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 75th Ed., inside cover, and specific functional groups are generally defined as described therein. Additionally, general principles of organic chemistry, as well as specific functional moieties and reactivity, are described in *Organic Chemistry*, Thomas Sorrell, University Science Books, Sausalito, 1999; Smith and March *March's Advanced Organic Chemistry*, 5th Edition, John Wiley & Sons, Inc., New York, 2001; Larock, *Comprehensive Organic Transformations*, VCH Publishers, Inc., New York, 1989; Carruthers, *Some Modern Methods of Organic Synthesis*, 3rd Edition,

Cambridge University Press, Cambridge, 1987; the entire contents of each of which are incorporated herein by reference.

[0043] The terms "halo" and "halogen" as used herein refer to an atom selected from fluorine (fluoro, –F), chlorine (chloro, –Cl), bromine (bromo, –Br), and iodine (iodo, –I).

[0044] The term "aliphatic" or "aliphatic group", as used herein, denotes a hydrocarbon moiety that may be straight–chain (i.e., unbranched), branched, or cyclic (including fused, bridging, and spiro–fused polycyclic) and may be completely saturated or may contain one or more units of unsaturation, but which is not aromatic. Unless otherwise specified, aliphatic groups contain 1–30 carbon atoms. In some embodiments, aliphatic groups contain 1–12 carbon atoms. In some embodiments, aliphatic groups contain 1–8 carbon atoms. In some embodiments, aliphatic groups contain 1–6 carbon atoms. In some embodiments, aliphatic groups contain 1–5 carbon atoms, in some embodiments, aliphatic groups contain 1–4 carbon atoms, in yet other embodiments aliphatic groups contain 1–3 carbon atoms, and in yet other embodiments, aliphatic groups contain 1–2 carbon atoms. Suitable aliphatic groups include, but are not limited to, linear or branched, alkyl, alkenyl, and alkynyl groups, and hybrids thereof such as (cycloalkyl)alkyl, (cycloalkenyl)alkyl or (cycloalkyl)alkenyl.

[0045] The term "heteroaliphatic," as used herein, refers to aliphatic groups wherein one or more carbon atoms are independently replaced by one or more atoms selected from the group consisting of oxygen, sulfur, nitrogen, phosphorus, or boron. In some embodiments, one or two carbon atoms are independently replaced by one or more of oxygen, sulfur, nitrogen, or phosphorus. Heteroaliphatic groups may be substituted or unsubstituted, branched or unbranched, cyclic or acyclic, and include "heterocycle," "heterocyclyl," "heterocycloaliphatic," or "heterocyclic" groups.

[0046] The term "acrylate" or "acrylates" as used herein refer to any acyl group having a vinyl group adjacent to the acyl carbonyl. The terms encompass mono-, di- and tri-substituted

vinyl groups. Examples of acrylates include, but are not limited to: acrylate, methacrylate, ethacrylate, cinnamate (3-phenylacrylate), crotonate, tiglate, and senecioate.

[0047] The term "polymer", as used herein, refers to a molecule of high relative molecular mass, the structure of which comprises the multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass. In some embodiments, a polymer is comprised of only one monomer species (e.g., polyethylene oxide). In some embodiments, a polymer is a copolymer, terpolymer, heteropolymer, block copolymer, or tapered heteropolymer of one or more epoxides.

[0048] The term "unsaturated", as used herein, means that a moiety has one or more double or triple bonds.

[0049] The terms "cycloaliphatic", "carbocycle", or "carbocyclic", used alone or as part of a larger moiety, refer to a saturated or partially unsaturated cyclic aliphatic monocyclic, bicyclic, or polycyclic ring systems, as described herein, having from 3 to 12 members, wherein the aliphatic ring system is optionally substituted as defined above and described herein. Cycloaliphatic groups include, without limitation, cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, cycloheptyl, cycloheptenyl, cyclooctyl, cyclooctenyl, and cyclooctadienyl. In some embodiments, the cycloalkyl has 3–6 carbons. The terms "cycloaliphatic", "carbocycle" or "carbocyclic" also include aliphatic rings that are fused to one or more aromatic or nonaromatic rings, such as decahydronaphthyl or tetrahydronaphthyl, where the radical or point of attachment is on the aliphatic ring. In some embodiments, a carbocyclic group is bicyclic. In some embodiments, a carbocyclic group is tricyclic. In some embodiments, a carbocyclic group is polycyclic.

[0050] The term "alkyl," as used herein, refers to saturated, straight– or branched–chain hydrocarbon radicals derived from an aliphatic moiety containing between one and six carbon atoms by removal of a single hydrogen atom. Unless otherwise specified, alkyl groups contain

1–12 carbon atoms. In some embodiments, alkyl groups contain 1–8 carbon atoms. In some embodiments, alkyl groups contain 1–6 carbon atoms. In some embodiments, alkyl groups contain 1–5 carbon atoms, in some embodiments, alkyl groups contain 1–4 carbon atoms, in yet other embodiments, alkyl groups contain 1–3 carbon atoms, and in yet other embodiments alkyl groups contain 1–2 carbon atoms. Examples of alkyl radicals include, but are not limited to, methyl, ethyl, n–propyl, isopropyl, n–butyl, iso–butyl, sec–butyl, sec–pentyl, iso–pentyl, tert–butyl, n–pentyl, neopentyl, n–hexyl, sec–hexyl, n–heptyl, n–octyl, n–decyl, n–undecyl, dodecyl, and the like.

[0051] The term "alkenyl," as used herein, denotes a monovalent group derived from a straight– or branched–chain aliphatic moiety having at least one carbon–carbon double bond by the removal of a single hydrogen atom. Unless otherwise specified, alkenyl groups contain 2–12 carbon atoms. In some embodiments, alkenyl groups contain 2–8 carbon atoms. In some embodiments, alkenyl groups contain 2–6 carbon atoms. In some embodiments, alkenyl groups contain 2–5 carbon atoms, in some embodiments, alkenyl groups contain 2–4 carbon atoms, in yet other embodiments, alkenyl groups contain 2–3 carbon atoms, and in yet other embodiments alkenyl groups contain 2 carbon atoms. Alkenyl groups include, for example, ethenyl, propenyl, butenyl, 1–methyl–2–buten–1–yl, and the like.

[0052] The term "alkynyl," as used herein, refers to a monovalent group derived from a straight– or branched–chain aliphatic moiety having at least one carbon–carbon triple bond by the removal of a single hydrogen atom. Unless otherwise specified, alkynyl groups contain 2–12 carbon atoms. In some embodiments, alkynyl groups contain 2–8 carbon atoms. In some embodiments, alkynyl groups contain 2–6 carbon atoms. In some embodiments, alkynyl groups contain 2–5 carbon atoms, in some embodiments, alkynyl groups contain 2–4 carbon atoms, in yet other embodiments alkynyl groups contain 2–3 carbon atoms, and in yet other

embodiments alkynyl groups contain 2 carbon atoms. Representative alkynyl groups include, but are not limited to, ethynyl, 2–propynyl (propargyl), 1–propynyl, and the like.

[0053] The term "carbocycle" and "carbocyclic ring" as used herein, refers to monocyclic and polycyclic moieties wherein the rings contain only carbon atoms. Unless otherwise specified, carbocycles may be saturated, partially unsaturated or aromatic, and contain 3 to 20 carbon atoms. Representative carbocyles include cyclopropane, cyclobutane, cyclopentane, cyclohexane, bicyclo[2,2,1]heptane, norbornene, phenyl, cyclohexene, naphthalene, and spiro[4.5]decane.

[0054] The term "aryl" used alone or as part of a larger moiety as in "aralkyl", "aralkoxy", or "aryloxyalkyl", refers to monocyclic and polycyclic ring systems having a total of five to 20 ring members, wherein at least one ring in the system is aromatic and wherein each ring in the system contains three to twelve ring members. The term "aryl" may be used interchangeably with the term "aryl ring". In some embodiments, "aryl" refers to an aromatic ring system which includes, but is not limited to, phenyl, naphthyl, anthracyl and the like, which may bear one or more substituents. Also included within the scope of the term "aryl", as it is used herein, is a group in which an aromatic ring is fused to one or more additional rings, such as benzofuranyl, indanyl, phthalimidyl, naphthimidyl, phenanthridinyl, or tetrahydronaphthyl, and the like.

[0055] The terms "heteroaryl" and "heteroar–", used alone or as part of a larger moiety, e.g., "heteroaralkyl", or "heteroaralkoxy", refer to groups having 5 to 14 ring atoms, preferably 5, 6, 9 or 10 ring atoms; having 6, 10, or 14 π electrons shared in a cyclic array; and having, in addition to carbon atoms, from one to five heteroatoms. The term "heteroatom" refers to nitrogen, oxygen, or sulfur, and includes any oxidized form of nitrogen or sulfur, and any quaternized form of a basic nitrogen. Heteroaryl groups include, without limitation, thienyl, furanyl, pyrrolyl, imidazolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, isothiazolyl, thiadiazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, indolizinyl,

purinyl, naphthyridinyl, benzofuranyl and pteridinyl. The terms "heteroaryl" and "heteroar–", as used herein, also include groups in which a heteroaromatic ring is fused to one or more aryl, cycloaliphatic, or heterocyclyl rings, where the radical or point of attachment is on the heteroaromatic ring. Non-limiting examples include indolyl, isoindolyl, benzothienyl, benzofuranyl, dibenzofuranyl, indazolyl, benzimidazolyl, benzthiazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, 4*H*–quinolizinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, phenoxazinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, and pyrido[2,3–b]–1,4–oxazin–3(4H)–one. A heteroaryl group may be monocyclic or bicyclic. The term "heteroaryl" may be used interchangeably with the terms "heteroaryl ring", "heteroaryl group", or "heteroaromatic", any of which terms include rings that are optionally substituted. The term "heteroaralkyl" refers to an alkyl group substituted by a heteroaryl, wherein the alkyl and heteroaryl portions independently are optionally substituted.

[0056] As used herein, the terms "heterocycle", "heterocyclyl", "heterocyclic radical", and "heterocyclic ring" are used interchangeably and refer to a stable 5– to 7–membered monocyclic or 7- to 14-membered bicyclic heterocyclic moiety that is either saturated or partially unsaturated, and having, in addition to carbon atoms, one or more, preferably one to four, heteroatoms, as defined above. When used in reference to a ring atom of a heterocycle, the term "nitrogen" includes a substituted nitrogen. As an example, in a saturated or partially unsaturated ring having 0–3 heteroatoms selected from oxygen, sulfur or nitrogen, the nitrogen may be N (as in 3,4–dihydro–2*H*–pyrrolyl), NH (as in pyrrolidinyl), or $^{+}$NR (as in *N*–substituted pyrrolidinyl).

[0057] A heterocyclic ring can be attached to its pendant group at any heteroatom or carbon atom that results in a stable structure and any of the ring atoms can be optionally substituted. Examples of such saturated or partially unsaturated heterocyclic radicals include, without limitation, tetrahydrofuranyl, tetrahydrothienyl, pyrrolidinyl, pyrrolidonyl, piperidinyl,

pyrrolinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, decahydroquinolinyl, oxazolidinyl, piperazinyl, dioxanyl, dioxolanyl, diazepinyl, oxazepinyl, thiazepinyl, morpholinyl, and quinuclidinyl. The terms "heterocycle", "heterocyclyl", "heterocyclyl ring", "heterocyclic group", "heterocyclic moiety", and "heterocyclic radical", are used interchangeably herein, and also include groups in which a heterocyclyl ring is fused to one or more aryl, heteroaryl, or cycloaliphatic rings, such as indolinyl, 3*H*–indolyl, chromanyl, phenanthridinyl, or tetrahydroquinolinyl, where the radical or point of attachment is on the heterocyclyl ring. A heterocyclyl group may be mono– or bicyclic. The term "heterocyclylalkyl" refers to an alkyl group substituted by a heterocyclyl, wherein the alkyl and heterocyclyl portions independently are optionally substituted.

[0058] As used herein, the term "partially unsaturated" refers to a ring moiety that includes at least one double or triple bond. The term "partially unsaturated" is intended to encompass rings having multiple sites of unsaturation, but is not intended to include aryl or heteroaryl moieties, as herein defined.

[0059] As described herein, compounds may contain "optionally substituted" moieties. In general, the term "substituted", whether preceded by the term "optionally" or not, means that one or more hydrogens of the designated moiety are replaced with a suitable substituent. Unless otherwise indicated, an "optionally substituted" group may have a suitable substituent at each substitutable position of the group, and when more than one position in any given structure may be substituted with more than one substituent selected from a specified group, the substituent may be either the same or different at every position. Combinations of substituents envisioned may include those that result in the formation of stable or chemically feasible compounds. The term "stable", as used herein, refers to compounds that are not substantially altered when subjected to conditions to allow for their production, detection, and,

in some embodiments, their recovery, purification, and use for one or more of the purposes disclosed herein.

[0060] In some chemical structures herein, substituents are shown attached to a bond which crosses a bond in a ring of the depicted molecule. This means that one or more of the substituents may be attached to the ring at any available position (usually in place of a hydrogen atom of the parent structure). In cases where an atom of a ring so substituted has two substitutable positions, two groups may be present on the same ring atom. When more than one substituent is present, each is defined independently of the others, and each may have a different structure. In cases where the substituent shown crossing a bond of the ring is –R, this has the same meaning as if the ring were said to be "optionally substituted" as described in the preceding paragraph.

[0061] Suitable monovalent substituents on a substitutable carbon atom of an "optionally substituted" group are independently halogen; $-(CH_2)_{0-4}R^\circ$; $-(CH_2)_{0-4}OR^\circ$; $-O-(CH_2)_{0-4}C(O)OR^\circ$; $-(CH_2)_{0-4}CH(OR^\circ)_2$; $-(CH_2)_{0-4}SR^\circ$; $-(CH_2)_{0-4}Ph$, which may be substituted with R°; $-(CH_2)_{0-4}O(CH_2)_{0-1}Ph$ which may be substituted with R°; –CH=CHPh, which may be substituted with R°; $-NO_2$; –CN; $-N_3$; $-(CH_2)_{0-4}N(R^\circ)_2$; $-(CH_2)_{0-4}N(R^\circ)C(O)R^\circ$; $-N(R^\circ)C(S)R^\circ$; $-(CH_2)_{0-4}N(R^\circ)C(O)NR^\circ_2$; $-N(R^\circ)C(S)NR^\circ_2$; $-(CH_2)_{0-4}N(R^\circ)C(O)OR^\circ$; $-N(R^\circ)N(R^\circ)C(O)R^\circ$; $-N(R^\circ)N(R^\circ)C(O)NR^\circ_2$; $-N(R^\circ)N(R^\circ)C(O)OR^\circ$; $-(CH_2)_{0-4}C(O)R^\circ$; $-C(S)R^\circ$; $-(CH_2)_{0-4}C(O)OR^\circ$; $-(CH_2)_{0-4}C(O)N(R^\circ)_2$; $-(CH_2)_{0-4}C(O)SR^\circ$; $-(CH_2)_{0-4}C(O)OSiR^\circ_3$; $-(CH_2)_{0-4}OC(O)R^\circ$; $-OC(O)(CH_2)_{0-4}SR^\circ$, –SC(S)SR°; $-(CH_2)_{0-4}SC(O)R^\circ$; $-(CH_2)_{0-4}C(O)NR^\circ_2$; $-C(S)NR^\circ_2$; –C(S)SR°; –SC(S)SR°, $-(CH_2)_{0-4}OC(O)NR^\circ_2$; $-C(O)N(OR^\circ)R^\circ$; $-C(O)C(O)R^\circ$; $-C(O)CH_2C(O)R^\circ$; $-C(NOR^\circ)R^\circ$; $-(CH_2)_{0-4}SSR^\circ$; $-(CH_2)_{0-4}S(O)_2R^\circ$; $-(CH_2)_{0-4}S(O)_2OR^\circ$; $-(CH_2)_{0-4}OS(O)_2R^\circ$; $-S(O)_2NR^\circ_2$; $-(CH_2)_{0-4}S(O)R^\circ$; $-N(R^\circ)S(O)_2NR^\circ_2$; $-N(R^\circ)S(O)_2R^\circ$; $-N(OR^\circ)R^\circ$; $-C(NH)NR^\circ_2$; $-P(O)_2R^\circ$; $-P(O)R^\circ_2$; $-OP(O)R^\circ_2$; $-OP(O)(OR^\circ)_2$; SiR°_3; –(C_{1-4} straight or branched alkylene)O–$N(R^\circ)_2$; or –(C_{1-4}

straight or branched alkylene)C(O)O–N(R°)$_2$, wherein each R° may be substituted as defined below and is independently hydrogen, C$_{1-8}$ aliphatic, –CH$_2$Ph, –O(CH$_2$)$_{0-1}$Ph, or a 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur, or, notwithstanding the definition above, two independent occurrences of R°, taken together with their intervening atom(s), form a 3–12–membered saturated, partially unsaturated, or aryl mono– or polycyclic ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur, which may be substituted as defined below.

[0062] Suitable monovalent substituents on R° (or the ring formed by taking two independent occurrences of R° together with their intervening atoms), are independently halogen, –(CH$_2$)$_{0-2}$R$^\bullet$, –(haloR$^\bullet$), –(CH$_2$)$_{0-2}$OH, –(CH$_2$)$_{0-2}$OR$^\bullet$, –(CH$_2$)$_{0-2}$CH(OR$^\bullet$)$_2$; -O(haloR$^\bullet$), –CN, –N$_3$, –(CH$_2$)$_{0-2}$C(O)R$^\bullet$, –(CH$_2$)$_{0-2}$C(O)OH, –(CH$_2$)$_{0-2}$C(O)OR$^\bullet$, -(CH$_2$)$_{0-4}$C(O)N(R°)$_2$; –(CH$_2$)$_{0-2}$SR$^\bullet$, –(CH$_2$)$_{0-2}$SH, –(CH$_2$)$_{0-2}$NH$_2$, –(CH$_2$)$_{0-2}$NHR$^\bullet$, -(CH$_2$)$_{0-2}$NR$^\bullet_2$, –NO$_2$, –SiR$^\bullet_3$, –OSiR$^\bullet_3$, –C(O)SR$^\bullet$, –(C$_{1-4}$ straight or branched alkylene)C(O)OR$^\bullet$, or –SSR$^\bullet$ wherein each R$^\bullet$ is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently selected from C$_{1-4}$ aliphatic, -CH$_2$Ph, –O(CH$_2$)$_{0-1}$Ph, or a 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur. Suitable divalent substituents on a saturated carbon atom of R° include =O and =S.

[0063] Suitable divalent substituents on a saturated carbon atom of an "optionally substituted" group include the following: =O, =S, =NNR$^*_2$, =NNHC(O)R*, =NNHC(O)OR*, =NNHS(O)$_2$R*, =NR*, =NOR*, –O(C(R$^*_2$))$_{2-3}$O–, or –S(C(R$^*_2$))$_{2-3}$S–, wherein each independent occurrence of R* is selected from hydrogen, C$_{1-6}$ aliphatic which may be substituted as defined below, or an unsubstituted 5–6–membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen,

and sulfur. Suitable divalent substituents that are bound to vicinal substitutable carbons of an "optionally substituted" group include: $-O(CR^*_2)_{2-3}O-$, wherein each independent occurrence of R^* is selected from hydrogen, C_{1-6} aliphatic which may be substituted as defined below, or an unsubstituted 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0064] Suitable substituents on the aliphatic group of R^* include halogen, $-R^\bullet$, -(halo$R^\bullet$), –OH, $-OR^\bullet$, –O(halo$R^\bullet$), –CN, –C(O)OH, $-C(O)OR^\bullet$, $-NH_2$, $-NHR^\bullet$, $-NR^\bullet_2$, or $-NO_2$, wherein each $R^\bullet$ is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently C_{1-4} aliphatic, $-CH_2Ph$, $-O(CH_2)_{0-1}Ph$, or a 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0065] Suitable substituents on a substitutable nitrogen of an "optionally substituted" group include $-R^\dagger$, $-NR^\dagger_2$, $-C(O)R^\dagger$, $-C(O)OR^\dagger$, $-C(O)C(O)R^\dagger$, $-C(O)CH_2C(O)R^\dagger$, $-S(O)_2R^\dagger$, $-S(O)_2NR^\dagger_2$, $-C(S)NR^\dagger_2$, $-C(NH)NR^\dagger_2$, or $-N(R^\dagger)S(O)_2R^\dagger$; wherein each $R^\dagger$ is independently hydrogen, C_{1-6} aliphatic which may be substituted as defined below, unsubstituted –OPh, or an unsubstituted 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur, or, notwithstanding the definition above, two independent occurrences of $R^\dagger$, taken together with their intervening atom(s) form an unsubstituted 3–12–membered saturated, partially unsaturated, or aryl mono– or bicyclic ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0066] Suitable substituents on the aliphatic group of $R^\dagger$ are independently halogen, $-R^\bullet$, –(halo$R^\bullet$), –OH, $-OR^\bullet$, –O(halo$R^\bullet$), –CN, –C(O)OH, $-C(O)OR^\bullet$, $-NH_2$, $-NHR^\bullet$, $-NR^\bullet_2$, or $-NO_2$, wherein each $R^\bullet$ is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently C_{1-4} aliphatic, $-CH_2Ph$, $-O(CH_2)_{0-1}Ph$, or a

5-6-membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0067] As used herein, the term "catalyst" refers to a substance the presence of which increases the rate of a chemical reaction, while not being consumed or undergoing a permanent chemical change itself.

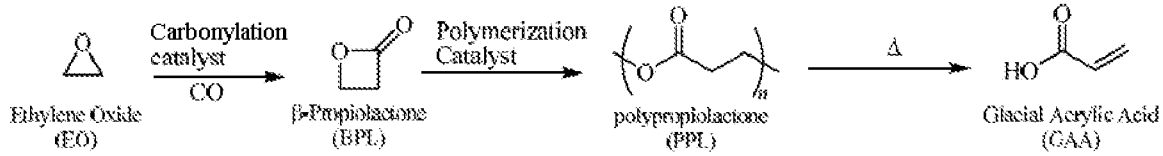
[0068] As used herein, the term "about" preceding one or more numerical values means the numerical value ±5%. It should be understood that reference to "about" a value or parameter herein includes (and describes) embodiments that are directed to that value or parameter per se. For example, description referring to "about x" includes description of "x" per se.

[0069] Further, it should be understood that reference to "between" two values or parameters herein includes (and describes) embodiments that include those two values or parameters per se. For example, description referring to "between x and y" includes description of "x" and "y" per se.

[0070] The mass fractions disclosed herein can be converted to wt% by multiplying by 100.

Glacial Acrylic Acid Production system/production process

[0071] Glacial acrylic acid can be produced from ethylene oxide and carbon monoxide according to the following general reaction scheme:



Ethylene oxide ("EO") may undergo a carbonylation reaction, *e.g.*, with carbon monoxide ("CO"), in the present of a carbonylation catalyst to produce β-propiolactone ("bPL"). The β-propiolactone may undergo polymerization in the presence of a polymerization catalyst to

produce polypropiolactone ("PPL"). The polypropiolactone may undergo thermolysis to produce glacial acrylic acid ("GAA").

[0072] PPL may undergo thermolysis by one of two primary reaction mechanisms as disclosed by (Iwabuchi, S., Jaacks, V., Galil, F. and Kern, W. (1973), The thermal degradation of poly(oxycarbonylethylene) (poly-β-propiolactone). Makromol. Chem., 165: 59–72). The desired mechanism is referred to as unzipping and it converts a PPL polymer with a chain length of "n" into one molecule of acrylic acid and reduces the PPL polymer chain length to n-1. The other method is referred to as chain scission; chain scission converts a PPL polymer of chain length n into a PPL polymer of chain length of less than n-2 and a PPL polymer of chain length of at least 2.

[0073] Product acrylic acid is susceptible to auto-polymerization via two mechanisms, either Michael addition or radical polymerization. Michael addition forms a product of two molecules of acrylic acid which is a di-acrylic acid ester and identical to a PPL of chain length 2. There is no known inhibitor of Michael addition of acrylic acid, but under thermolysis conditions this reaction is reversible and can decompose back into two molecules of acrylic acid. The product of Radical polymerization of acrylic acid produces polyacrylic acid, and will not normally convert back into acrylic acid under thermolysis conditions. There are many known inhibitors for radical polymerization of acrylic acid, including but not limited to phenothiazine (PTZ) and 4-methoxyphenol (MEHQ). Under many circumstances, a stream of radical polymerization inhibitor (either neat or in appropriate solvent) is added in batch or continuous mode to the primary thermolysis reactor or mixed with PPL stream before introduction to reactor to combat losses of acrylic acid to polyacrylic acid in thermolysis reactor.

[0074] Thermolysis of PPL may be catalyzed by the presence of a depolymerization catalyst. Depolymerization catalyst (either neat or in appropriate solvent) may be added in

batch or continuous mode to the primary thermolysis reactor or mixed with PPL stream before introduction to reactor to reduce severity of thermolysis reaction conditions (which reduces conversion of acrylic acid to polyacrylic acid). Optimally, the catalyst employed for bPL polymerization can be used as a depolymerization catalyst as well. The thermolysis reactor can be designed (see below) such that the concentrations of the polymerization catalyst species in the PPL inlet stream and in the thermolysis reactor, which along with the difference in reactor conditions and stream compositions accounts for the seemingly divergent functions.

[0075] Provided herein are systems and methods for the production of glacial acrylic acid from ethylene oxide and carbon monoxide on an industrial scale. For example, in some aspects, the systems and methods described herein are suitable for the production of glacial acrylic acid on a scale of 25 kilo tons per annum ("KTA"). In some variations, the systems provided herein are configured to produce glacial acrylic acid in a continuous process, and further feedback loops to continually produce acrylic acid.

[0076] Further, in some variations, the systems provided herein further include various purification systems to produce glacial acrylic acid of high purity. For example, the systems provided herein may be configured to remove residual carbonylation catalyst, carbonylation solvent, and by-products (*e.g.*, acetaldehyde, succinic anhydride, and acrylic acid dimer) to achieve glacial acrylic acid with a purity of at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%.

[0077] In other variations, the systems provided herein are also configured to recycle various starting materials and glacial acrylic acid precursors, such as poly-propiolactone. For example, the systems may include one or more recycle systems to isolate unreacted ethylene oxide, unreacted carbon monoxide, carbonylation solvent, and catalyst.

[0078] In yet other variations, the systems provided herein are also configured to manage and integrate heat produced. The carbonylation reaction to produce β-propiolactone and the

polymerization reaction to produce polypropiolactone are exothermic. Thus, the heat generated from the exothermic unit operations, such as the carbonylation reactor and polymerization reactor can be captured and used for cooling in endothermic unit operations, such as the distillation apparatus and thermolysis reactor. For example, in some variations of the systems and methods provided herein, steam may be generated in heat transfer equipment (*e.g.*, shell and tube heat exchanger and reactor cooling jacket) via a temperature gradient between process fluid and water/steam. This steam can be used for heat integration between exothermic and endothermic unit operations. In other variations of the systems and methods provided herein, other suitable heat transfer fluids may be used.

[0079] In other variations, heat integration may be achieved by combining certain unit operations. For example, heat integration may be achieved by combining polymerization of β-propiolactone and vaporization of the solvent (*e.g.*, THF) from the distillation column within a single unit operation. In such a configuration, the heat liberated from the β-propiolactone polymerization reaction is used directly to vaporize the solvent in the distillation apparatus, and the output of the unit produces polypropiolactone. In other variations, the heat liberated from the polymerization reaction can be exported to other systems at the same production site.

[0080] With reference to FIG. **1**, an exemplary system to produce acrylic acid from carbon monoxide and ethylene oxide is depicted. Carbon monoxide (CO), a carbonylation catalyst, ethylene oxide (EO) and carbonylation solvent are fed into a β-propiolactone production system/production process, depicted as a continuous stirred tank reactor (CSTR) in FIG. **1**. Such β-propiolactone production system/production process is typically configured to produce a liquid product stream of β-propiolactone. This β-propiolactone product stream is fed to an EO/CO separator, depicted as the flash tank in FIG. **1**, where unreacted ethylene oxide and unreacted carbon monoxide may be separated and recycled for use in the CSTR. The β-propiolactone product stream is then fed from the EO/CO separator to a carbonylation catalyst

recycle system, depicted as a nanofilter in FIG. **1**. The carbonylation catalyst recycle system is configured to separate residual carbonylation catalyst present in the β-propiolactone product stream, and such separated carbonylation catalyst may be recycled for use in the CSTR. The nanofilter depicted in FIG. **1** may be any suitable membrane, such as a polymeric membrane or a ceramic membrane, and produces a retentate stream typically made up of β-propiolactone, carbonylation solvent, residual carbonylation catalyst, small amounts of ethylene oxide, carbon monoxide, and by-products (such as acetaldehyde and succinic anhydride), and a permeate stream typically made up of β-propiolactone, carbonylation solvent, small amounts of ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and succinic anhydride) and trace amounts of carbonylation catalyst. In some embodiments, trace amount is less than 1% by wt, less than 0.5% by wt, less than 0.01% by wt, less than 0.005% by wt, less than 0.001% by wt, or less than 0.0001% by wt. In certain embodiments, trace amount is below the detection threshold of the measurement method being used.

[0081] The permeate is fed into a β-propiolactone purification system, depicted as a distillation column in FIG. **1**, which is configured to separate ethylene oxide, carbon monoxide, and by-products from the solvent recycle stream, which is depicted as a tetrahydrofuran (THF) recycle stream. The system in FIG. **1** depicts the use of THF as the carbonylation solvent, but it should be understood that in other variations, other suitable solvents may be used. The purified β-propiolactone stream from the β-propiolactone purification system and polymerization catalyst are fed into a polypropiolactone production system/production process, depicted as a plug flow reactor in FIG. **1**. The polypropiolactone production system/production process is configured to produce a polypropiolactone product stream, which can be fed into a thermolysis reactor to produce glacial acrylic acid.

[0082] It should be understood, however, that while FIG. **1** depicts an exemplary glacial acrylic acid production system/production process, variations of this productions system are

envisioned. For example, while a CSTR is depicted as the reactor in the β-propiolactone production system/production process, other reactors and reactor configurations may be employed. In another example, while a distillation column and a plug flow reactor are depicted in FIG. **1** in the β-propiolactone purification system and polypropiolactone productions system, respectively, other separation apparatuses and other reactors and reactor configurations may be employed.

[0083] Additionally, in other exemplary embodiments of the systems described herein, various unit operations depicted in FIG. **1** may be combined or omitted. In some variations, the β-propiolactone production system/production process and membrane unit operations may be combined (e.g. membrane reactor) or polymerization and depolymerization may be combined (e.g. catalytic or reactive distillation) may be combined, or the EO/CO separator may be omitted.

[0084] Further, it should be understood that in other exemplary embodiments of systems described herein, additional unit operations may be employed. For example, in some embodiments it may be possible to incorporate one or more ion exchange resins into the systems to remove various cationic and anionic catalyst species that may result from the use of the carbonylation catalyst. In other embodiments, one or more heat exchangers may be incorporated into the systems to manage and integrate heat produced in the system.

[0085] In yet other embodiments the process and/or system by which it is practiced may employ a variety of sensors and control equipment to automate control of the process and any related system. For example, the various reactors, in particular a β-propiolactone reactor, used in the process and any related system may employ a sensor to detect amounts of water and oxygen in the reactor or that enters the reactor. Such sensor may be connected to a control that can adjust parameters to maintain water and oxygen content under a predefined amount. Such sensor may monitor the carbonylation catalyst to detect amounts of water and oxygen in the

reactor and may be connected to a control that can control the amount of carbonylation catalyst from the carbonylation catalyst source. In addition, or alternatively the carbon monoxide source may comprise a sensor configured to detect amounts of water and oxygen in the reactor and such sensor may be connected to a control that can control the amount of carbon monoxide from the carbon monoxide source. In addition, or alternatively the ethylene oxide source may comprises a sensor configured to detect amounts of water and oxygen in the reactor and such sensor may be connected to a control that can control the amount of ethylene oxide from the ethylene oxide source.

[0086] Provided herein are various systems configured for the commercial production of polypropiolactone (PPL) and glacial acrylic acid (GAA). In some configurations, PPL and GAA are produced at the same geographical location. In other configurations, PPL is produced in one location and shipped to a second location where GAA is produced.

[0087] In other variations of such configurations, the residual carbonylation catalyst (which may include cationic and anionic species) may be removed at various points in the production system/production process. For example, in certain configurations, the residual carbonylation catalyst may be removed from the PPL product stream prior to thermolysis to produce GAA. In other configurations, the residual carbonylation catalyst may be removed, if desired to do so, after thermolysis by distillation or other separation means.

[0088] In yet other variations, β-propiolactone (bPL) may be polymerized to produce PPL by way of complete conversion of bPL. In such a variation, there may not be a need for additional apparatus in the system to isolate and recycle bPL to the polymerization reactor. In other variations, the conversion of bPL is not complete. Unreacted bPL may be separated from the PPL product stream and the recovered bPL may be recycled back to the polymerization reactor.

[0089] These variations in the configurations of the systems are described in further detail with respect to FIGS. **6-13**. FIG. **6** depicts an exemplary system wherein the PPL product stream and the GAA product stream are produced at the same location, at least a portion of the carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, and the polypropiolactone production system/production process is configured to achieve complete conversion of bPL to PPL.

[0090] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0091] The BPL production system/production process (labeled 'Carbonylation' in FIG. **6**) typically includes a carbon monoxide (CO) source, an ethylene oxide (EO) source, a carbonylation catalyst source, a solvent source, and a carbonylation reactor. In certain variations, the carbonylation reactor is configured to receive carbon monoxide (CO), ethylene oxide (EO), and solvent from a CO source, an EO source, and a solvent source (collectively labeled 'Feed Stock Delivery' in FIG. **6**). The carbonylation reactor is further configured to receive a carbonylation catalyst from a carbonylation catalyst source (labeled 'CO Catalyst Delivery' in FIG. **6**). The carbon monoxide, ethylene oxide, carbonylation solvent, and carbonylation catalyst may be obtained by any commercially available sources, or any commercially available methods and techniques known in the art.

[0092] In some variations, the CO, EO, and solvent are essentially water and oxygen free. In one variation, the solvent from the solvent source, the EO from the EO source, and the CO

from the CO source have a concentration of water and oxygen less than about 500 ppm, less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, less than about 10 ppm, less than about 2 ppm, or less than 1 ppm.

[0093] Any suitable carbonylation solvents may be used. In some embodiments, the carbonylation solvent comprises tetrahydrofuran, hexane, or a combination thereof. In other embodiments, the carbonylation solvent comprises an ether, a hydrocarbon, or a combination thereof. In yet other embodiments, the carbonylation solvent comprises tetrahydrofuran, tetrahydropyran, 2,5-dimethyl tetrahydrofuran, sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, propyl acetate, butyl acetate, 2-butanone, cyclohexanone, toluene, difluorobenzene, dimethoxy ethane, acetone, or methylethyl ketone, or any combination thereof. In one variation, the carbonylation solvent comprises tetrahydrofuran.

[0094] The carbonylation catalyst used herein may be made on-site and/or off-site. In some embodiments, the carbonylation catalyst is a cobalt-aluminum catalyst. In certain embodiments, the carbonylation catalyst comprises a carbonyl cobaltate in combination with an aluminum porphyrin compound, a carbonyl cobaltate in combination with an aluminum salen compound, or a carbonyl cobaltate in combination with an aluminum salophen compound. In one variation, the carbonylation catalyst is $(Al(TPP)Co(CO)_4)$.

[0095] The carbonylation reactor may be a continuous reactor, such as a continuous stirred tank reactor (CSTR). Other reactors described herein, such as batch reactors, plug flow reactors (PFR), and semi-batch reactors may also be employed.

[0096] With reference again to the exemplary system in FIG. **6**, the carbonylation reactor may be configured to receive EO from the EO source at any rate, temperature, or pressure

described herein. For example, in some embodiments, the inlet to the carbonylation reactor receives EO from an EO source at about 1000 kg/hr to 25000 kg/hr. In some embodiments, the inlet to the carbonylation reactor receives EO from an EO source at about 30 kmol/hr to about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reactor is configured to receive EO from an EO source at a temperature between about 10°C to about 30°C. In some embodiments, the inlet to the carbonylation reactor is configured to receive EO from an EO source at a pressure between about 20 bar to about 100 bar and in a more narrow range 50 bar to 70 bar.

[0097] With reference again to the exemplary system in FIG. **6**, the carbonylation reactor may be configured to receive CO from the CO source at any rate, temperature, or pressure described herein. For example, in some embodiments, the inlet to the carbonylation reactor is configured to receive CO from a CO source at a temperature between about 10°C to about 170°C and more narrowly between 10°C to about 70°C. In some embodiments, the inlet to the carbonylation reactor is configured to receive CO from a CO source at a pressure between about 20 bar to about 100 bar and more narrowly 50 and 70 bar. In some embodiments, the CO source that supplies CO to the carbonylation reactor is a fresh carbon monoxide source (i.e., main CO feed), or recycled carbon monoxide from the β-propiolactone production system/production process, or a combination thereof. In some embodiments, the fresh CO source is configured to provide between about 1000 kg/hr CO to about 16000 kg/hr CO. In some embodiments, the fresh CO source is configured to provide between about 30 kmol/hr CO to about 600 kmol/hr CO. In some embodiments, the recycled CO from the β-propiolactone production system/production process can provide between about 100 kg/hr CO to about 3500 kg/hr CO. In some embodiments, the recycled CO source is configured to provide between about 3 kmol/hr CO to about 150 kmol/hr CO.

[0098] With reference again to the exemplary system in FIG. **6**, the carbonylation reactor may be configured to receive solvent at any rate, temperature, or pressure described herein. For example, in some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at a rate of between about 10000 kg/hr to about 130000 kg/hr. In some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at rate of between about 150 kmol/hr to about 1900 kmol/hr. In some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at a temperature between about 10°C to about 160°C and more narrowly 10°C to about 60°C. In some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at a pressure of between about 20 bar to about 100 bar and more narrowly 50 bar to 65 bar. In some embodiments, the solvent feed that supplies solvent to the carbonylation reactor can include solvent from a fresh solvent source, recycled solvent from the BPL purification system (e.g., BPL distillation system), and/or solvent in the recycled carbonylation catalyst stream from the carbonylation catalyst recycle system.

[0099] In some embodiments, the pressure in the carbonylation reactor is about 900 psig, and the temperature is about 70°C. In certain variations, the reactor is equipped with an external cooler (heat exchanger). In some variations, the carbonylation reaction achieves a selectivity of bPL above 99%.

[00100] With reference again to the exemplary system in FIG. **6**, a β-propiolactone product stream exits the outlet of the carbonylation reactor. The β-propiolactone product stream comprises bPL, solvent, unreacted EO and CO, carbonylation catalyst, and by-products, such as acetaldehyde by-product (ACH) and succinic anhydride (SAH). The β-propiolactone product stream may have any concentration of bPL, solvent, EO, CO carbonylation catalyst, ACH, and SAH described herein. For example, in some embodiments, the β-propiolactone product stream includes between about 2000 kg/hr bPL to about 40000 kg/hr bPL. In some

embodiments, the β-propiolactone product stream includes between about 30 kmol/hr bPL to about 550 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the β-propiolactone product stream can be about 0.1 to about 0.4. In some embodiments, the mole fraction of bPL in the β-propiolactone product stream can be about 0.1 to about 0.6. and more narrowly 0.1 to 0.4. The β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005 to 0.15, or at most about 0.1), unreacted carbon monoxide (in mass fraction of about 0.0005 to 0.04, or at most about 0.02), acetaldehyde (in mass fraction of about 0.0005 to 0.01, or at most about 0.02), succinic anhydride (in mass fraction of about 0.0005 to 0.005, or at most about 0.01), carbonylation catalyst (in about 40 to 640 kg/hr, or at most about 600 kg/hr; or a mass fraction of about 0.001 to 0.005, or at most about 0.004), and the remainder solvent. In some embodiments, the β-propiolactone product stream comprises carbonylation catalyst components (in about 40 to 640 kg/hr, or at most about 600 kg/hr; or a mass fraction of about 0.001 to 0.005, or at most about 0.004). In some embodiments, the β-propiolactone product stream from the β-propiolactone production system/production process can have a temperature of about 40°C or 50°C to about 100°C, and a pressure of about 1 bar to about 15 bar or more narrowly to 5 bar.

[00101] With reference again to the exemplary system in FIG. **6**, the β-propiolactone product stream is output from an outlet of the carbonylation reactor and enters an inlet of the ethylene oxide and carbon monoxide separator (labeled 'EO/CO' in FIG. **6**). In one embodiment, the ethylene oxide and carbon monoxide separator is a flash tank. The majority of the ethylene oxide and carbon monoxide is recovered from the carbonylation reaction stream and can be recycled back to the carbonylation reactor as a recycled ethylene oxide stream and a recycled carbon monoxide stream (labeled 'Recycle' in FIG. **6**), or sent for disposal (labeled 'Flare' in FIG. **6**). In some embodiments, at least 10% of the ethylene oxide and 80% of the carbon monoxide in the carbonylation reaction stream is recovered. The recycled carbon

monoxide stream can also include unreacted ethylene oxide (in about at most 250 kg/hr or a mass fraction of between about 0.05 to about 0.075), secondary reaction product acetaldehyde (in at most about 13 kg/hr or a mass fraction of about 0.001 to about 0.009), bPL (in at most about 0.19 kg/hr), and the remainder solvent (e.g., THF).

[00102] With reference again to the exemplary system in FIG. **6**, the β-propiolactone product stream is pumped into the carbonylation catalyst recycle system. In some variations, the ethylene oxide and carbon monoxide are disposed of using a method other than flare. For example, in one embodiment, the ethylene oxide and carbon monoxide recovered from the β-propiolactone product stream are disposed of using incineration.

[00103] With reference again to the exemplary system in FIG. **6**, the β-propiolactone product stream enters an inlet of the carbonylation catalyst recycling system. The carbonylation catalyst recycling system may be configured to isolate at least a portion of the carbonylation catalyst from the β-propiolactone product stream using any of the methods described herein, including, for example distillation, liquid-liquid extraction, ionic liquids, nanofiltration, ion exchange, or adsorption, or any combinations thereof. In some variations, the carbonylation catalyst recycling system includes a membrane separator. In certain variations, the membrane separator comprises a polymeric membrane, while in other variations the membrane separator comprises a ceramic membrane. In some variations, the membrane of the catalyst recycle system is configured to achieve between 90% and 100% rejection of the catalyst, and have permeability greater than 1. In some embodiments the membrane is achieves greater than 90%, 92%, 95%, 98%, or 99% rejection of the catalyst.

[00104] The carbonylation catalyst recycling system is configured to produce a recycled carbonylation catalyst stream (labeled 'Retentate' in FIG. **6**) comprising bPL, solvent, ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and carbonylation catalyst) and carbonylation catalyst, and a post-isolation β-propiolactone product stream (labeled 'Permeate'

in FIG. **6**) comprising bPL, solvent, ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and succinic anhydride) and trace amounts of carbonylation catalyst. In some embodiments, the post-isolation β-propiolactone product stream comprises trace amounts of carbonylation catalyst components. In some embodiments, trace amount is less than 1% by wt, less than 0.5% by wt, less than 0.01% by wt, less than 0.005% by wt, less than 0.001% by wt, or less than 0.0001% by wt. In certain embodiments, trace amount is below the detection threshold of the measurement method being used.

[00105] The recycled carbonylation catalyst stream may comprise any concentration of carbonylation catalyst, carbonylation catalyst components, and solvent disclosed herein. For example, in some embodiments, the mass fraction of carbonylation catalyst in the recycled carbonylation catalyst stream is about 0.005 to about 0.05. In some embodiments, the mass fraction of carbonylation catalyst components in the recycled carbonylation catalyst stream is about 0.0051 to about 0.05. In some embodiments, the mole fraction of carbonylation catalyst in the recycled carbonylation catalyst stream is about 0.0005 to about 0.05. In some embodiments, the mole fraction of carbonylation catalyst components in the recycled carbonylation catalyst stream is about 0.0005 to about 0.05. In some embodiments, the mass fraction of solvent in the recycled carbonylation catalyst stream is between 0.60 to about 0.99. In some embodiments, the mole fraction of solvent in the recycled carbonylation catalyst stream is between about 0.60 to about 0.99. In some embodiments, the recycled carbonylation catalyst stream can also include unreacted carbon monoxide (in at most about 15 kg/hr or a mass fraction of at most about 0.001), unreacted ethylene oxide (in at most about 330 kg/hr or a mass fraction of between 0.005 to 0.01), secondary reaction product acetaldehyde (in at most about 33 kg/hr or a mass fraction of at most about 0.001), secondary reaction product succinic anhydride (in at most about 30 kg/hr or a mass fraction of at most about 0.001), bPL (in at

most about 5450 kg/hr or a mass fraction of at most about 0.25). The recycled carbonylation catalyst stream is recycled back to the carbonylation reactor.

[00106] The post-isolation β-propiolactone product stream may have any concentration of bPL, solvent, ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and succinic anhydride), carbonylation catalyst, or carbonylation catalyst components described herein. For example, in some embodiments, the post-isolation β-propiolactone product stream includes about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the post-isolation β-propiolactone product stream includes about 30 kmol/hr bPL to about 450 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1 to 0.4, or the mole fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1 to about 0.4. The post-isolation β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005 to 0.1), unreacted carbon monoxide (in mass fraction of about 0.0005 to 0.001, or at most about 0.002), acetaldehyde (in mass fraction of about 0.0005 to 0.001, or at most about 0.002), succinic anhydride (in mass fraction of about 0.0005 to 0.01, or at most about 0.02), carbonylation catalyst (in about 0 to 50 kg/hr, or at most about 20 kg/hr), carbonylation catalyst components (in about 0 to 50 kg/hr, or at most about 20 kg/hr) and the remainder solvent. In some embodiments, the post-isolation β-propiolactone product stream from the carbonylation catalyst recycling system can have a temperature of about 20°C to about 60°C. In some embodiments, the post-isolation β-propiolactone product stream can have a pressure of about 1 to about 5 bar.

[00107] With reference again to the exemplary system in FIG. **6**, the post-isolation β-propiolactone product stream may enter the inlet of the BPL purification system (labeled 'BPL Distillation' in FIG. **6**). In one variation, the BPL purification system comprises one or more distillation columns operating at or below atmospheric pressure configured to produce a

recovered solvent stream, and a production stream comprising purified bPL and trace amounts of carbonylation catalyst (labeled 'BPL/residual cat.' in FIG. **6**). The pressure is selected in such a way to achieve the temperature that reduces the decomposition of bPL. In some embodiments, the one or more distillation columns are operated at a pressure of about 0.15 bara and a temperature between about 80°C and about 120°C. In some embodiments, the distillation system is configured to produce a recycled solvent stream essentially free of ethylene oxide, carbon monoxide, acetaldehyde, and succinic anhydride.

[0100] With reference again to the exemplary system in FIG. **6**, the recovered solvent stream exits an outlet of the BPL purification system and may be fed back to the carbonylation reactor. In some variations, the concentration of H_2O and O_2 is reduced in the recycled solvent stream prior to being fed to the carbonylation reactor. The recovered solvent stream may have any concentration of H_2O and O_2 described herein when fed back to the carbonylation reactor. For example, in some embodiments, the concentration of H_2O and O_2 is less than about 500 ppm, less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, less than about 20 ppm, less than about 10 ppm, less than about 2 ppm, or less than about 1 ppm when fed back into the carbonylation reactor.

[0101] With reference again to the exemplary system in FIG. **6**, the production stream comprising purified bPL exits the outlet of the BPL purification system. The production stream may contain trace amounts of carbonylation catalyst, but is essentially free of solvent, ethylene oxide, carbon monoxide, acetaldehyde, and succinic anhydride. In some embodiments, the production stream contains a mass fraction of bPL of about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the production stream is about 0.90 to 1.0. In some embodiments, the remainder of the production stream includes secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or from 0 to 0.0015), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments,

the remainder of the production stream includes carbonylation catalyst components (in at most about 1000 ppm).

[0102] The production stream enters an inlet of the polypriolactone production system/production process. In the exemplary system depicted in FIG. **6**, the polypriolactone production system/production process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **6**). The polypriolactone production system/production process is configured to receive and output streams at any rate, concentration, temperature, or pressure described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or from 0 to about 0.015), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). The remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm).In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80°C to 120°C. In some embodiments, the production stream exiting the distillation process can be at a pressure of about 0.05 bar to about 0.15 bar. In some embodiments, the production stream entering the polymerization process can be at a pressure of at least about 0.05 bar, at least about 1 bar, or at least about 5 bar, or between about 0.05 bar and about 20 bar.

[0103] With reference again to the exemplary system in FIG. **6**, the polypropiolactone production system/production process is configured to operate in a continuous mode and achieves complete conversion of bPL in the production stream to PPL. A PPL product stream (labeled 'PPL/residual cat.' in FIG. **6**) exits an outlet of the polypropiolactone production system/production process, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises trace amount of carbonylation catalyst components.

[0104] In some embodiments, the polymerization process is configured to produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process is configured to produce about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0105] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or between 0 and 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or between 0 and 0.01) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the PPL product stream can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the PPL product stream can have a temperature between about 100°C to 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0106] With reference again to the exemplary system in FIG. **6**, the PPL product stream enters an inlet of the PPL purification system (labeled 'IER' in FIG. **6**). The PPL purification system can comprises and ion exchange resin (IER) configured to reduce the concentration of carbonylation catalyst in the PPL product stream. The cationic and anionic carbonylation catalyst species are recovered from the IER in the PPL purification system and can be

regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **6**). A post-purification PPL product stream exits an outlet of the PPL purification system and enters an inlet of the thermolysis reactor. The post-purification PPL product stream may have any concentration of compounds, temperature, or pressure described herein. For example, in some embodiments, the mass fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the post-purification PPL product stream can have a temperature between about 100°C to 140°C. In some embodiments, the post-purification PPL product stream can be at a pressure of at least about 0.001 bar.

[0107] With reference again to the exemplary system in FIG. **6**, a thermolysis reactor is configured to convert the post-purification PPL stream to a GAA product stream. In some embodiments, the temperature of the thermolysis reactor is between 140 °C or 160 °C and 300°C and the pressure is between 0.1 bara and 5 bara.

[0108] Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **6**) are separated from the GAA stream, exit an outlet of the thermolysis reactor, and sent to the incinerator for disposal (labeled 'Incinerator' in FIG. **6**).

[0109] A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 50°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 bar to about 1.5 bar.

[0110] The exemplary production system/production process depicted in FIG. **6** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA") to about 250 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0111] FIG. **7** provides an exemplary production system/production process where the PPL product stream and the GAA product stream are produced at the same location, at least a portion of the carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, and the conversion of bPL in the production stream to PPL in the polymerization reactor is incomplete, with recycling of bPL back to the polymerization reactor. The production system/production process shown in FIG. **7** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system as shown in FIG. **6**.

[0112] With reference again to the exemplary system in FIG. **7**, the production stream comprising purified bPL exits the outlet of the BPL purification system. The production stream may contain trace amounts of carbonylation catalyst, but is essentially free of solvent, ethylene oxide, carbon monoxide, acetaldehyde, and succinic anhydride. In some embodiments, the production stream contains a mass fraction of bPL of about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the production stream is about 0.90 to 1.0. In some embodiments, the remainder of the production stream includes secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the

remainder of the production stream includes carbonylation catalyst components (in at most about 1000 ppm).

[0113] With reference again to the exemplary system in FIG. **7**, the polypropiolactone production system/production process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **7**) and a BPL recycling system (labeled 'Distill/WFE' in FIG. **7**). The polypropiolactone production system/production process may be configured to receive and output streams at any rate, concentration, temperature, or pressure of production stream described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or 0 to 0.015) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80 to 120°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of about 0.05 bar to about 20 bar.

[0114] With reference again to the exemplary system in FIG. **7**, the PPL production system/production process is configured to operate in a continuous mode, achieving partial

conversion of bPL to PPL. The PPL production system/production process may be configured to achieve various levels of bPL conversion. For example, in some embodiments, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% of the bPL in the production stream is converted to PPL. In some embodiments, about 50% to about 99% of the bPL in the production stream is converted to PPL. The partial polymerization stream exits the outlet of the polymerization reactor and enters the inlet of the BPL recycling system. The BPL recycling system is configured to separate unreacted bPL from the partial polymerization stream and recycle the bPL back into the polymerization reactor (labeled 'bPL' in FIG. **7**). In some embodiments, the BPL recycling system comprises one or more distillation columns, while in other embodiments the BPL recycling system comprises one or more wiped-film evaporators (WFE). A PPL product stream (labeled 'PPL/residual cat.' in FIG. **7**) exits the outlet of the BPL recycling system, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises PPL with trace amount of carbonylation catalyst components. In some embodiments, the polymerization process can produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process can produce about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0115] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or 0 to 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or from 0 to 0.01) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the PPL product stream can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the PPL product stream can

have a temperature between about 100 °C to 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0116] The PPL product stream enters the inlet of the PPL purification system (labeled 'IER' in FIG. **7**). In some variations, the PPL purification system may use an ion exchange resin (IER) to reduce the concentration of carbonylation catalyst in the PPL product stream. The cationic and anionic carbonylation catalyst species are recovered from the IER in the PPL purification system and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **7**). A post-purification PPL product stream exits an outlet of the PPL purification system and enters an inlet of the thermolysis reactor. The post-purification PPL product stream may have any concentration of compounds, temperature, or pressure described herein. For example, in some embodiments, the mass fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the post-purification PPL product stream can have a temperature between about 100°C to about 140°C. In some embodiments, the post-purification PPL product stream can be at a pressure of at least about 0.001 bar.

[0117] With reference again to the exemplary system in FIG. **7**, the glacial acrylic acid production system/production process is configured to convert the post-purification PPL stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **7**) are output via an outlet of the thermolysis reactor, and are sent to the incinerator for disposal (labeled 'Incinerator' in FIG. **7**). A GAA product stream exits an outlet of the thermolysis reactor, and may be condensed, further processed or stored. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary

reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 bar to about 1.5 bar.

[0118] The exemplary production system/production process depicted in FIG. **7** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA") to about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0119] FIG. **8** depicts an exemplary production system/production process where the PPL product stream and the GAA product stream are produced at the same location, carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor, the conversion of bPL to PPL in the polymerization process is complete with no recycling of bPL to the polymerization process, and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor. The production system/production process in FIG. **8** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system as shown in FIG. **6**.

[0120] With reference again to the exemplary system in FIG. **8**, the production stream exits the outlet of the BPL purification system and enters the inlet of the polymerization process. In the production system/production process depicted in FIG. **8**, the polymerization process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **8**). An inlet to the polymerization process may include any rate, concentration, temperature, or pressure of

production stream described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or 0 to 0.015), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80°C to about 120°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of about 0.05 bar to about 0.15 bar.

[0121] With reference again to the exemplary system in FIG. **8**, the polypropiolactone production system/production process is configured to operate in a continuous mode, achieving complete conversion of bPL in the production stream to PPL. A PPL product stream (labeled 'PPL/residual cat.' in FIG. **8**) exits the polymerization process outlet, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises PPL with trace amount of carbonylation catalyst components.

[0122] In some embodiments, the polymerization process can produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process can produce about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0123] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or from 0 to 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or from 0 to 0.01), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the PPL product stream can have a temperature between about 100°C to about 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0124] With reference again to the exemplary system in FIG. **8**, the PPL product stream enters the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **8**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **8**) comprising ion exchange resin (IER) which may be used in some embodiments may be useful. The IER is configured to reduce the concentration of carbonylation catalyst in the stream of high boiling organic impurities. In some embodiments, the concentration of carbonylation catalyst in the stream of high boiling organic impurities is between 100 ppm to 1000 ppm before entering the purification system, and is less than 50 ppm, less than 20 ppm, or less than 5 ppm after exiting the purification system.

[0125] The cationic and anionic carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **8**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. A GAA product stream exits an outlet of the thermolysis

reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0126] The exemplary production system/production process depicted in FIG. **8** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA to about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0127] FIG. **9** depicts an exemplary production system/production process where the PPL product stream and the GAA product stream are produced at the same location, carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor, the conversion of bPL to PPL in the polymerization process is in complete and bPL is recycled back to the polymerization process, and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor. The production system/production process in FIG. **9** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system as shown in FIG. **6**.

[0128] With reference again to the exemplary system in FIG. **9**, the production stream comprising purified bPL exits the outlet of the BPL purification system. The production stream

contains trace amounts of carbonylation catalyst, but is essentially free of THF, EO, CO, ACH, and SAH. The production stream is fed forward and enters an inlet of the polymerization process. The polymerization process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **9**) and a BPL recycling system (labeled 'Distill/WFE' in FIG. **9**). An inlet to the polymerization process may include any rate, concentration, temperature, or pressure of production stream described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or from 0 to 0.015) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80°C to 120°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of about 0.05 bar to about 20 bar.

[0129] With reference again to the exemplary system in FIG. **9**, the polypropiolactone production system/production process is configured to operate in a continuous mode, achieving partial conversion of bPL in the production stream to PPL. The polypropiolactone production system/production process may be configured to achieve various levels of bPL conversion. For example, in some embodiments, at least 40%, at least 50%, at least 60%, at least 70%, at least

80%, or at least 90% of the bPL in the production stream is converted to PPL. In some embodiments, about 50% to about 95% of the bPL in the production stream is converted to PPL. In some embodiments, about 50% to about 99% of the bPL in the production stream is converted to PPL. The partial polymerization stream exits the outlet of the polymerization reactor and enters the inlet of the BPL recycling system. The BPL recycling system is configured to separate unreacted bPL from the partial polymerization stream and recycle the bPL back into the polymerization reactor (labeled 'bPL' in FIG. **9**). In some embodiments, the BPL recycling system comprises one or more distillation columns, while in other embodiments the BPL recycling system comprises one or more wiped-film evaporators (WFE). A PPL product stream (labeled 'PPL/residual cat.' in FIG. **9**) exits the outlet of the BPL recycling system, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises PPL with trace amount of carbonylation catalyst components. In some embodiments, the polymerization process is configured to produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process is configured to produce from about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0130] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or from 0 to 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or from 0 to 0.01), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the PPL product stream can have a temperature between about 100°C to 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0131] With reference again to the exemplary system in FIG. **9**, the PPL product stream enters the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **9**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **9**) comprising ion exchange resin (IER). The IER is configured to reduce the concentration of carbonylation catalyst (or components thereof) in the stream of high boiling organic impurities. The cationic and anionic carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **9**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and leftover solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0132] The exemplary production system/production process depicted in FIG. 9 may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA and about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0133] FIG. **10** depicts another exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, the polymerization reactor achieves complete conversion of bPL in the production stream to PPL and bPL is not recycled back to the polymerization reactor. The production system/production process in FIG. **10** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, polymerization process, PPL purification system, and regeneration or disposal of carbonylation catalyst components as shown in FIG. **6**.

[0134] With reference again to the exemplary system in FIG. **10**, the post-purification PPL product stream exits an outlet of the PPL purification system and is pelletized, extruded, flaked, powdered, or granulated by any means known in the art in essentially dry atmosphere. The solid post-purification PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid post-purification PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid post-purification PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the post-isolation PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **10**) are output via an outlet of the thermolysis reactor and sent to an incinerator for disposal (labeled 'Incinerator' in FIG. **10**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product

stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0135] The exemplary production system/production process depicted in FIG. **10** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA and about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0136] FIG. **11** depicts an exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, the polymerization reactor achieves incomplete conversion of bPL in the production stream to PPL and bPL is recycled back to the polymerization reactor. The production system/production process in FIG. **11** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, polymerization process, PPL purification system, and regeneration or disposal of carbonylation catalyst components as shown in FIG. **7**.

[0137] With reference again to the exemplary system in FIG. **11**, the post-purification PPL product stream exits an outlet of the PPL purification system and is pelletized, extruded, flaked, powdered, or granulated by means known in the art in essentially dry atmosphere. The solid

post-purification PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid post-purification PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid post-purification PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the post-isolation PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **11**) are output via an outlet of the thermolysis reactor and sent to an incinerator for disposal (labeled 'Incinerator' in FIG. **11**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0138] The exemplary production system/production process depicted in FIG. **11** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA to about 250 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0139] FIG. **12** depicts another exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor; the polymerization reactor achieves complete conversion of bPL in the production stream to PPL and bPL is not recycled back to the polymerization reactor; and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor. The production system/production process in FIG. **12** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, and polymerization process as shown in FIG. **8**.

[0140] With reference again to the exemplary system in FIG. **12**, the PPL product stream exits an outlet of the polymerization process and is pelletized, extruded, flaked, powdered, or granulated by means known in the art in essentially dry atmosphere. The solid PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **12**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **12**) comprising ion exchange and which is an example of one separation the may be employed. The IER is configured to reduce the concentration of carbonylation catalyst (or components thereof) in the stream of high boiling organic impurities. The cationic and anionic

carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **12**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. In preferred embodiment the temperature is controlled to limit the risk of autopolymerization of acrylic acid. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0141] The exemplary production system/production process depicted in FIG. **12** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA and about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0142] FIG. **13** depicts an exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor; the polymerization reactor achieves incomplete conversion of bPL in the production stream to PPL and bPL is recycled back to the polymerization reactor; and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor.

The production system/production process in FIG. **13** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, and polymerization process as shown in FIG. **9**.

[0143] With reference again to the exemplary system in FIG. **13**, the PPL product stream exits an outlet of the polymerization process and is pelletized, extruded, flaked, powdered, or granulated by means known in the art in essentially dry atmosphere. The solid PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **13**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **13**) comprising ion exchange resin (IER). The IER is configured to reduce the concentration of carbonylation catalyst (or components thereof) in the stream of high boiling organic impurities. The cationic and anionic carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **13**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream

can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0144] The exemplary production system/production process depicted in FIG. **13** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), at least about 100 KTA, at least about 110 KTA, at least about 120 KTA, at least about 130 KTA, at least about 140 KTA, at least about 150 KTA, at least about 160 KTA, at least about 170 KTA, at least about 180 KTA, at least about 190 KTA, at least about 200 KTA, at least about 250 KTA, at least about 300 KTA, at least about 350 KTA, at least about 400 KTA, and in some variations that may be combined with any of the preceding variations, up to about 400 KTA, for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0145] It should be understood that while FIGS. **6-13** depict process configurations comprising certain steps and unit operations, in other embodiments of the methods described herein the process configuration contains fewer steps, more steps, fewer unit operations, or more unit operations. For example, in some variations, the permeate stream is treated to remove at least a portion of the trace carbonylation catalyst prior to the BPL purification train. In certain variations, it may be possible toremove of at least a portion of the trace carbonylation catalyst from the permeate with an ion exchange resin. Thus, in certain embodiments, the process configurations in FIGS. **6-13** includes the additional step of removing at least a portion of the trace carbonylation catalyst from the permeate using IER, before the permeate enters the BPL purification train. In some embodiments, the systems depicted in FIGS. **6-13** and described herein include a purification system with IER before prior to the BPL purification

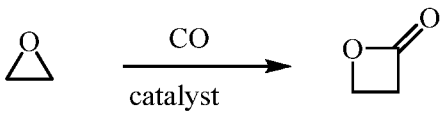
train. In other embodiments, the systems include a purification system with IER prior to the BPL purification train and use a heterogeneous polymerization catalyst in the polymerization process. In some embodiments, the systems do not have a purification system after the polymerization process.

[0146] Each of the unit operations in the production system/production processs for acrylic acid and precursors thereof are described in further detail below.

β-Propiolactone Production system/production process (i.e., carbonylation reaction system)

[0147] FIG. **14** illustrates an exemplary embodiment of the production system/production process disclosed herein. FIG. **14** contains carbonylation reaction system 1413 (i.e., β-propiolactone production system/production process), catalyst isolation system 1415, BPL purification system 1417, polymerization reaction system 1419, and thermolysis system 1421.

[0148] In the carbonylation reaction system, Ethylene oxide can be converted to β-propiolactone by a carbonylation reaction, as depicted in the reaction scheme below.



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[0149] Water and oxygen can damage the carbonylation catalyst. The feed streams (i.e., EO, CO, solvent, carbonylation catalyst) to the carbonylation reaction system should be substantially dry (i.e., have a water content below 5 ppm) and be oxygen free (i.e., have an oxygen content below 5 ppm). As such, the feed streams and/or storage tanks and/or feed tank can have sensors on them in order to determine the composition of the stream/tank to make sure that they have a low enough oxygen and water content. In some embodiments, the feed streams can be purified such as by adsorption to reduce the water and oxygen content in the streams fed to the carbonylation reaction system. In some embodiments, prior to running the production system/production process, the tubes, apparatuses, and other flow paths can be

purged with an inert gas or carbon monoxide to minimize exposure to oxygen or water in the production system/production process.

Ethylene Oxide Source

[0150] FIG. **14** includes ethylene oxide source 1402 that can feed fresh ethylene oxide in ethylene oxide stream 1406 to carbonylation reaction system inlet 1409. Inlet 1409 can be one inlet to the carbonylation reaction system or multiple inlets. Ethylene oxide can be fed as a liquid using a pump or any other means known to those of ordinary skill in the art. In addition, the ethylene oxide source can be maintained under an inert atmosphere. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at least about 1000 kg/hr, at least about 1500 kg/hr, at least about 2000 kg/hr, at least about 2070 kg/hr, or at least about 2500 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 1000 kg/hr to about 2500 kg/hr, at least about 1500 kg/hr to about 2500 kg/hr, at least about 2000 kg/hr to about 2500 kg/hr, or at least about 2070 kg/hr to about 2500 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source from about 1000 kg/hr to about 25000 kg/hr, about 1500 kg/hr to about 25000 kg/hr, about 2000 kg/hr to about 25000 kg/hr, about 2500 kg/hr to about 25000 kg/hr, about 5000 kg/hr to about 25000 kg/hr, about 7500 kg/hr to about 25000 kg/hr, about 10000 kg/hr to about 25000 kg/hr, about 12500 kg/hr to about 25000 kg/hr, about 15000 kg/hr to about 25000 kg/hr, about 17500 kg/hr to about 25000 kg/hr, about 20000 kg/hr to about 25000 kg/hr, or about 22500 kg/hr to about 25000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 1000 kg/hr, about 1500 kg/hr, about 2000 kg/hr, about 2070 kg/hr, about 2500 kg/hr, about 3000 kg/hr, about 3500 kg/hr, about 4000 kg/hr, about 4500 kg/hr, about 5000 kg/hr, 7500 kg/hr, about 10000 kg/hr, about 12500 kg/hr, about 15000 kg/hr, about 17500 kg/hr, about

20000 kg/hr, about 22500 kg/hr, or about 25000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at least about 30 kmol/hr, at least about 35 kmol/hr, at least about 40 kmol/hr, at least about 47 kmol/hr, at least about 50 kmol/hr, at least about 100 kmol/hr, at least about 200 kmol/hr, at least about 300 kmol/hr, at least about 400 kmol/hr, or at least about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 30 kmol/hr to about 500 kmol/hr, about 35 kmol/hr to about 500 kmol/hr, about 40 kmol/hr to about 500 kmol/hr, about 47 kmol/hr to about 500 kmol/hr, about 50 kmol/hr to about 500 kmol/hr, about 100 kmol/hr to about 500 kmol/hr, about 200 kmol/hr to about 500 kmol/hr, about 300 kmol/hr to about 500 kmol/hr, or about 400 kmol/hr to about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 30 kmol/hr, about 35 kmol/hr, about 40 kmol/hr, about 47 kmol/hr, about 50 kmol/hr, about 70 kmol/hr, about 80 kmol/hr about 90 kmol/hr, about 100 kmol/hr, about 150 kmol/hr, about 200 kmol/hr, about 250 kmol/hr, about 300 kmol/hr, about 350 kmol/hr, about 400 kmol/hr, about 450 kmol/hr, or about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at a temperature between about 10-30°C, between about 15-25°C, or about 20°C. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Carbonylation Catalyst Source

[0151] Numerous carbonylation catalysts known in the art are suitable for (or can be adapted to) methods of the present invention. For example, in some embodiments, the carbonylation methods utilize a metal carbonyl-Lewis acid catalyst such as those described in U.S. Patent No. 6,852,865. In other embodiments, the carbonylation step is performed with

one or more of the carbonylation catalysts disclosed in U.S. Patent Application Serial Nos. 10/820,958; and 10/586,826. In other embodiments, the carbonylation step is performed with one or more of the catalysts disclosed in U.S. Patent Nos. 5,310,948; 7,420,064; and 5,359,081. Additional catalysts for the carbonylation of epoxides are discussed in a review in Chem. Commun., 2007, 657–674. The entirety of each of the preceding references is incorporated herein by reference.

[0152] In some embodiments, the carbonylation catalyst includes a metal carbonyl compound. Typically, a single metal carbonyl compound is provided, but in some embodiments, mixtures of two or more metal carbonyl compounds are provided. Thus, when a provided metal carbonyl compound "comprises", e.g., a neutral metal carbonyl compound, it is understood that the provided metal carbonyl compound can be a single neutral metal carbonyl compound, or a neutral metal carbonyl compound in combination with one or more metal carbonyl compounds. Preferably, the provided metal carbonyl compound is capable of ring-opening an epoxide and facilitating the insertion of CO into the resulting metal carbon bond. Metal carbonyl compounds with this reactivity are well known in the art and are used for laboratory experimentation as well as in industrial processes such as hydroformylation.

[0153] In some embodiments, a provided metal carbonyl compound comprises an anionic metal carbonyl moiety. In other embodiments, a provided metal carbonyl compound comprises a neutral metal carbonyl compound. In some embodiments, a provided metal carbonyl compound comprises a metal carbonyl hydride or a hydrido metal carbonyl compound. In some embodiments, a provided metal carbonyl compound acts as a pre-catalyst which reacts *in situ* with one or more reaction components to provide an active species different from the compound initially provided. Such pre-catalysts are specifically encompassed as it is recognized that the active species in a given reaction may not be known with certainty; thus

the identification of such a reactive species *in situ* does not itself depart from the spirit or teachings of the present disclosure.

[0154] In some embodiments, the metal carbonyl compound comprises an anionic metal carbonyl species. In some embodiments, such anionic metal carbonyl species have the general formula $[Q_dM'_e(CO)_w]^{y-}$, where Q is any ligand and need not be present, M' is a metal atom, *d* is an integer between 0 and 8 inclusive, *e* is an integer between 1 and 6 inclusive, *w* is a number such as to provide the stable anionic metal carbonyl complex, and *y* is the charge of the anionic metal carbonyl species. In some embodiments, the anionic metal carbonyl has the general formula $[QM'(CO)_w]^{y-}$, where Q is any ligand and need not be present, M' is a metal atom, *w* is a number such as to provide the stable anionic metal carbonyl, and *y* is the charge of the anionic metal carbonyl.

[0155] In some embodiments, the anionic metal carbonyl species include monoanionic carbonyl complexes of metals from groups 5, 7 or 9 of the periodic table or dianionic carbonyl complexes of metals from groups 4 or 8 of the periodic table. In some embodiments, the anionic metal carbonyl compound contains cobalt or manganese. In some embodiments, the anionic metal carbonyl compound contains rhodium. Suitable anionic metal carbonyl compounds include, but are not limited to: $[Co(CO)_4]^-$, $[Ti(CO)_6]^{2-}$ $[V(CO)_6]^-$ $[Rh(CO)_4]^-$, $[Fe(CO)_4]^{2-}$ $[Ru(CO)_4]^{2-}$, $[Os(CO)_4]^{2-}$ $[Cr_2(CO)_{10}]^{2-}$ $[Fe_2(CO)_8]^{2-}$ $[Tc(CO)_5]^-$ $[Re(CO)_5]^-$and $[Mn(CO)_5]^-$. In some embodiments, the anionic metal carbonyl comprises $[Co(CO)_4]^-$. In some embodiments, a mixture of two or more anionic metal carbonyl complexes may be present in the carbonylation catalysts used in the methods.

[0156] The term "such as to provide a stable anionic metal carbonyl" for $[Q_dM'_e(CO)_w]^{y-}$ is used herein to mean that $[Q_dM'_e(CO)_w]^{y-}$ is a species characterizable by analytical means, e.g., NMR, IR, X-ray crystallography, Raman spectroscopy and/or electron spin resonance (EPR) and isolable in catalyst form in the presence of a suitable cation or a species formed *in*

situ. It is to be understood that metals which can form stable metal carbonyl complexes have known coordinative capacities and propensities to form polynuclear complexes which, together with the number and character of optional ligands Q that may be present and the charge on the complex will determine the number of sites available for CO to coordinate and therefore the value of *w*. Typically, such compounds conform to the "18-electron rule". Such knowledge is within the grasp of one having ordinary skill in the arts pertaining to the synthesis and characterization of metal carbonyl compounds.

[0157] In embodiments where the provided metal carbonyl compound is an anionic species, one or more cations must also necessarily be present. In some variations, no particular constraints on the identity of such cations. In some embodiments, the cation associated with an anionic metal carbonyl compound comprises a reaction component of another category described herein. For example, in some embodiments, the metal carbonyl anion is associated with a cationic Lewis acid. In other embodiments a cation associated with a provided anionic metal carbonyl compound is a simple metal cation such as those from Groups 1 or 2 of the periodic table (e.g., Na^+, Li^+, K^+, Mg^{2+} and the like). In other embodiments a cation associated with a provided anionic metal carbonyl compound is a bulky non electrophilic cation such as an 'onium salt' (e.g., Bu_4N^+, PPN^+, Ph_4P^+ Ph_4As^+, and the like). In other embodiments, a metal carbonyl anion is associated with a protonated nitrogen compound (e.g., a cation may comprise a compound such as MeTBD-H^+, DMAP-H^+, DABCO-H^+, DBU-H^+ and the like). In some embodiments, compounds comprising such protonated nitrogen compounds are provided as the reaction product between an acidic hydrido metal carbonyl compound and a basic nitrogen-containing compound (e.g., a mixture of DBU and $HCo(CO)_4$).

[0158] In some embodiments, a catalyst utilized in the methods described herein comprises a neutral metal carbonyl compound. In some embodiments, such neutral metal carbonyl compounds have the general formula $Q_dM'_e(CO)_{w'}$, where Q is any ligand and need not be

present, M' is a metal atom, *d* is an integer between 0 and 8 inclusive, e is an integer between 1 and 6 inclusive, and *w'* is a number such as to provide the stable neutral metal carbonyl complex. In some embodiments, the neutral metal carbonyl has the general formula $QM'(CO)_{w'}$. In some embodiments, the neutral metal carbonyl has the general formula $M'(CO)_{w'}$. In some embodiments, the neutral metal carbonyl has the general formula $QM'_2(CO)_{w'}$. In some embodiments, the neutral metal carbonyl has the general formula $M'_2(CO)_{w'}$. Suitable neutral metal carbonyl compounds include, but are not limited to: $Ti(CO)_7$; $V_2(CO)_{12}$; $Cr(CO)_6$; $Mo(CO)_6$; $W(CO)_6$ $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ $Fe(CO)_5$, $Ru(CO)_5$ and $Os(CO)_5$ $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Ir_4(CO)_{12}$ $Co_2(CO)_8$ $Ni(CO)_4$.

[0159] The term "such as to provide a stable neutral metal carbonyl" for $Q_dM'_e(CO)_{w'}$ is used herein to mean that $Q_dM'_e(CO)_{w'}$ is a species characterizable by analytical means, e.g., NMR, IR, X-ray crystallography, Raman spectroscopy and/or electron spin resonance (EPR) and isolable in pure form or a species formed *in situ*. It is to be understood that metals which can form stable metal carbonyl complexes have known coordinative capacities and propensities to form polynuclear complexes which, together with the number and character of optional ligands Q that may be present will determine the number of sites available for CO to coordinate and therefore the value of *w'*. Typically, such compounds conform to stoichiometries conforming to the "18-electron rule". Such knowledge is within the grasp of one having ordinary skill in the arts pertaining to the synthesis and characterization of metal carbonyl compounds.

[0160] In some embodiments, no ligands Q are present on the metal carbonyl compound. In other embodiments, one or more ligands Q are present on the metal carbonyl compound. In some embodiments, where Q is present, each occurrence of Q is selected from the group consisting of phosphine ligands, amine ligands, cyclopentadienyl ligands, heterocyclic ligands,

nitriles, phenols, and combinations of two or more of these. In some embodiments, one or more of the CO ligands of any of the metal carbonyl compounds described above is replaced with a ligand Q. In some embodiments, Q is a phosphine ligand. In some embodiments, Q is a triaryl phosphine. In some embodiments, Q is trialkyl phosphine. In some embodiments, Q is a phosphite ligand. In some embodiments, Q is an optionally substituted cyclopentadienyl ligand. In some embodiments, Q is cp. In some embodiments, Q is cp*. In some embodiments, Q is an amine or a heterocycle.

[0161] In some embodiments, the carbonylation catalyst utilized in the methods described above further includes a Lewis acidic component. In some embodiments, the carbonylation catalyst includes an anionic metal carbonyl complex and a cationic Lewis acidic component. In some embodiments, the metal carbonyl complex includes a carbonyl cobaltate and the Lewis acidic co-catalyst includes a metal-centered cationic Lewis acid. In some embodiments, an included Lewis acid comprises a boron compound.

[0162] In some embodiments, where an included Lewis acid comprises a boron compound, the boron compound comprises a trialkyl boron compound or a triaryl boron compound. In some embodiments, an included boron compound comprises one or more boron-halogen bonds. In some embodiments, where an included boron compound comprises one or more boron-halogen bonds, the compound is a dialkyl halo boron compound (e.g., R_2BX), a dihalo monoalkyl compound (e.g., RBX_2), an aryl halo boron compound (e.g., Ar_2BX or $ArBX_2$), or a trihalo boron compound (e.g., BCl_3 or BBr_3), wherein each R is an alkyl group; each X is a halogen; and each Ar is an aromatic group.

[0163] In some embodiments, where the included Lewis acid comprises a metal-centered cationic Lewis acid, the Lewis acid is a cationic metal complex. In some embodiments, the cationic metal complex has its charge balanced either in part, or wholly by one or more anionic metal carbonyl moieties. Suitable anionic metal carbonyl compounds include those described

above. In some embodiments, there are 1 to 17 such anionic metal carbonyls balancing the charge of the metal complex. In some embodiments, there are 1 to 9 such anionic metal carbonyls balancing the charge of the metal complex. In some embodiments, there are 1 to 5 such anionic metal carbonyls balancing the charge of the metal complex. In some embodiments, there are 1 to 3 such anionic metal carbonyls balancing the charge of the metal complex.

[0164] In some embodiments, where carbonylation catalysts used in systems and methods described herein include a cationic metal complex, the metal complex has the formula $[(L^c)_vM_b]^{z+}$, where:

L^c is a ligand where, when two or more L^c are present, each may be the same or different;

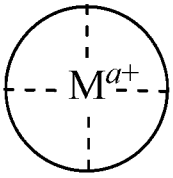
M is a metal atom where, when two M are present, each may be the same or different;

v is an integer from 1 to 4 inclusive;

b is an integer from 1 to 2 inclusive; and

z is an integer greater than 0 that represents the cationic charge on the metal complex.

[0165] In some embodiments, provided Lewis acids conform to structure **I**:



I

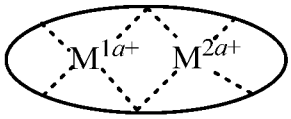
wherein:

 is a multidentate ligand;

M is a metal atom coordinated to the multidentate ligand;

a is the charge of the metal atom and ranges from 0 to 2; and

In some embodiments, provided metal complexes conform to structure **II**:



II

Where *a* is as defined above (each *a* may be the same or different), and

M^1 is a first metal atom;

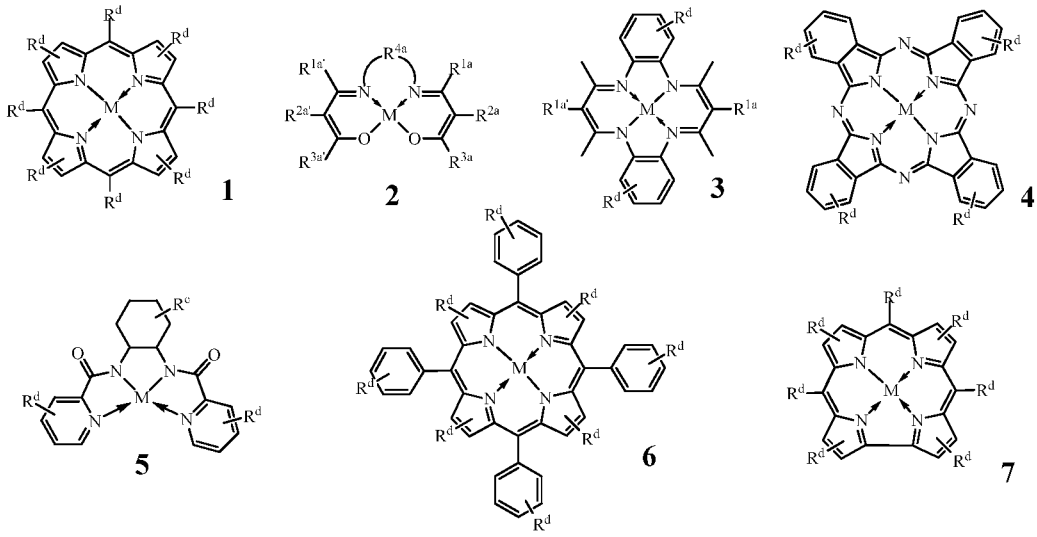
M^2 is a second metal atom;

 comprises a multidentate ligand system capable of coordinating both metal atoms.

[0166] For sake of clarity, and to avoid confusion between the net and total charge of the metal atoms in complexes **I** and **II** and other structures herein, the charge (a^+) shown on the metal atom in complexes **I** and **II** above represents the *net* charge on the metal atom after it has satisfied any anionic sites of the multidentate ligand. For example, if a metal atom in a complex of formula **I** were Cr(III), and the ligand were porphyrin (a tetradentate ligand with a charge of -2), then the chromium atom would have a net charge of +1, and *a* would be 1.

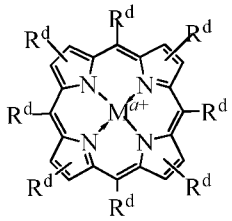
[0167] Suitable multidentate ligands include, but are not limited to: porphyrin derivatives **1**, salen derivatives **2**, dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives **3**, phthalocyaninate derivatives **4**, derivatives of the Trost ligand **5**, tetraphenylporphyrin derivatives **6**, and corrole derivatives **7**. In some embodiments, the multidentate ligand is a salen derivative. In other embodiments, the multidentate ligand is a porphyrin derivative. In other embodiments, the multidentate ligand is a tetraphenylporphyrin derivative. In other

embodiments, the multidentate ligand is a corrole derivative.



where each of R^c, R^d, R^{1a}, R^{2a}, R^{3a}, R^{4a}, $R^{1a'}$, $R^{2a'}$, $R^{3a'}$, and M, is as defined and described in the classes and subclasses herein.

[0168] In some embodiments, Lewis acids provided carbonylation catalysts used in systems and methods described herein comprise metal-porphinato complexes. In some embodiments, the moiety  has the structure:



where each of M and *a* is as defined above and described in the classes and subclasses herein, and

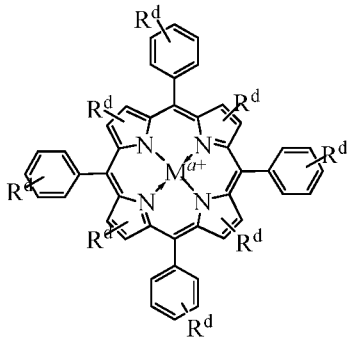
R^d at each occurrence is independently hydrogen, halogen, $-OR^4$, $-NR^y_2$, $-SR^y$, -CN, $-NO_2$, $-SO_2R^y$, $-SOR^y$, $-SO_2NR^y_2$; -CNO, $-NR^ySO_2R^y$, -NCO, $-N_3$, $-SiR^y_3$; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group

consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur, where two or more R^d groups may be taken together to form one or more optionally substituted rings,

each R^y is independently hydrogen, an optionally substituted group selected the group consisting of acyl; carbamoyl, arylalkyl; 6- to 10-membered aryl; C_{1-12} aliphatic; C_{1-12} heteroaliphatic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; an oxygen protecting group; and a nitrogen protecting group; two R^y on the same nitrogen atom are taken with the nitrogen atom to form an optionally substituted 4- to 7-membered heterocyclic ring having 0-2 additional heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; and

each R^4 is independently is a hydroxyl protecting group or R^y.

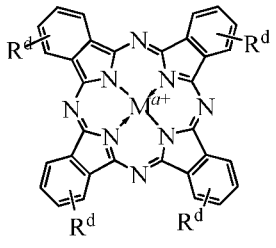
[0169] In some embodiments, the moiety  has the structure:



,

where M, *a* and R^d are as defined above and in the classes and subclasses herein.

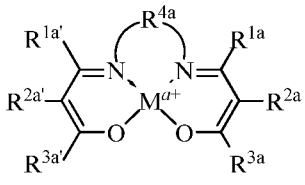
In some embodiments, the moiety  has the structure:



,

where M, *a* and R^d are as defined above and in the classes and subclasses herein.

[0170] In some embodiments, Lewis acids included in carbonylation catalysts used in systems and methods described herein comprise metallo salenate complexes. In some embodiments, the moiety  has the structure:



,

wherein:

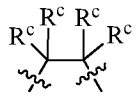
M, and *a* are as defined above and in the classes and subclasses herein.

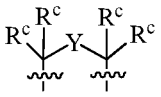
R^{1a}, $R^{1a'}$, R^{2a}, $R^{2a'}$, R^{3a}, and $R^{3a'}$ are independently hydrogen, halogen, $-OR^4$, $-NR^y_2$, $-SR^y$, -CN, $-NO_2$, $-SO_2R^y$, $-SOR^y$, $-SO_2NR^y_2$; -CNO, $-NR^ySO_2R^y$, -NCO, $-N_3$, $-SiR^y_3$; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; wherein each R^4,

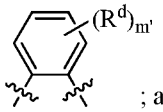
and R^y is independently as defined above and described in classes and subclasses herein,

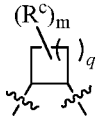
wherein any of ($R^{2a'}$ and $R^{3a'}$), (R^{2a} and R^{3a}), (R^{1a} and R^{2a}), and ($R^{1a'}$ and $R^{2a'}$) may optionally be taken together with the carbon atoms to which they are attached to form one or more rings which may in turn be substituted with one or more R^y groups; and

R^{4a} is selected from the group consisting of:

e) 

f) 

g)  ; and

h)  , where

R^c at each occurrence is independently hydrogen, halogen, $-OR^4$, $-NR^y_2$, $-SR^y$, -CN, $-NO_2$, $-SO_2R^y$, $-SOR^y$, $-SO_2NR^y_2$; -CNO, $-NR^ySO_2R^y$, -NCO, $-N_3$, $-SiR^y_3$; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur;

where:

two or more R^c groups may be taken together with the carbon atoms to which they are attached and any intervening atoms to form one or more rings;

when two R^c groups are attached to the same carbon atom, they may be taken together along with the carbon atom to which they are attached to form a moiety selected from the group consisting of: a 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, an imine; and an optionally substituted alkene;

where R^4 and R^y are as defined above and in classes and subclasses herein;

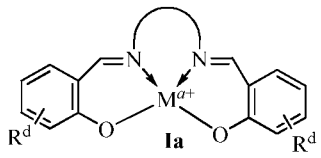
Y is a divalent linker selected from the group consisting of: $–NR^y$-, -$N(R^y)C(O)$-, -$C(O)NR^y$-, –O-, –C(O)-, –OC(O)-, -C(O)O-, -S-, -SO-, -SO_2-, -C(=S) -, -$C(=NR^y)$-, -N=N-; a polyether; a C_3 to C_8 substituted or unsubstituted carbocycle; and a C_1 to C_8 substituted or unsubstituted heterocycle;

m' is 0 or an integer from 1 to 4, inclusive;

q is 0 or an integer from 1 to 4, inclusive; and

x is 0, 1, or 2.

[0171] In some embodiments, a provided Lewis acid comprises a metallo salen compound, as shown in formula **Ia**:



Ia

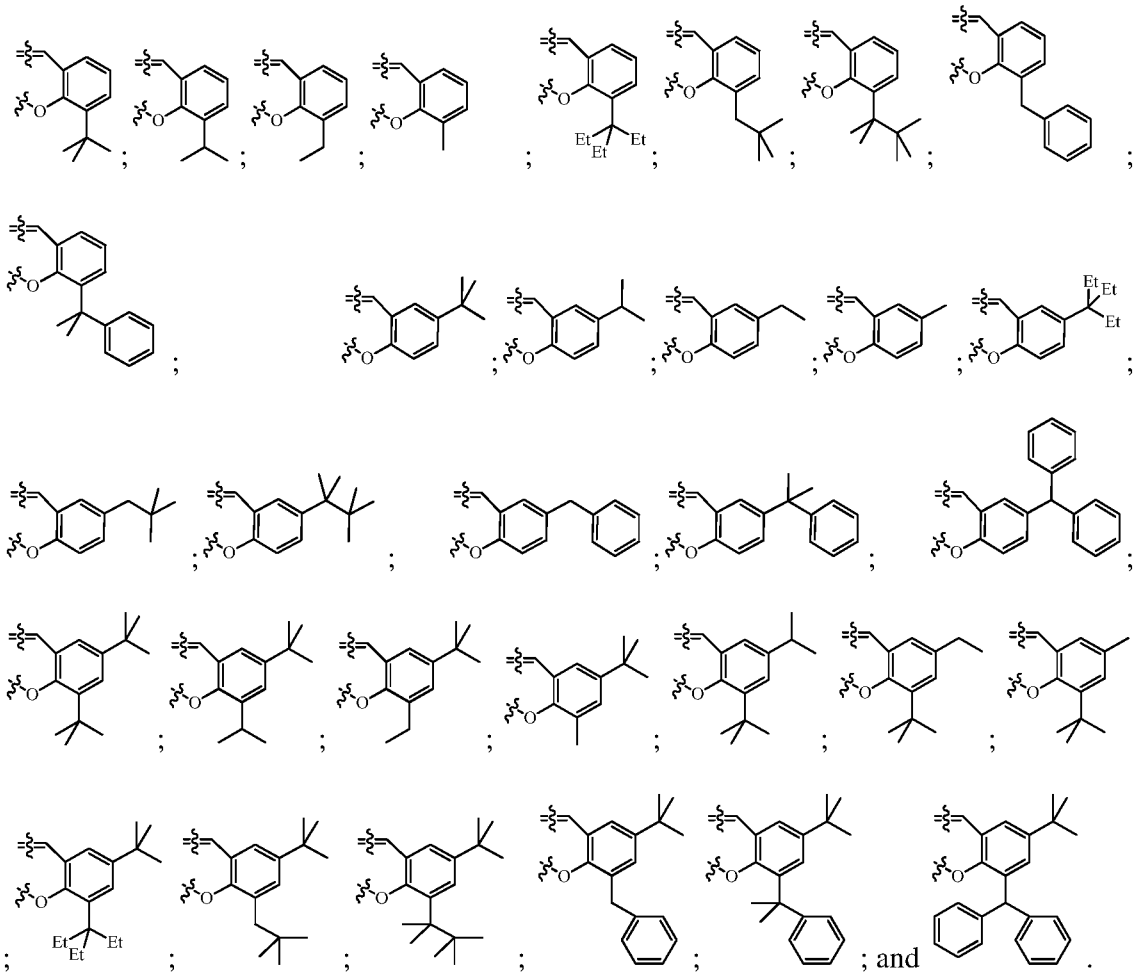
,

wherein each of M, R^d, and *a*, is as defined above and in the classes and subclasses herein,

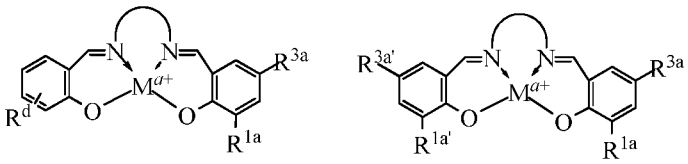
 represents is an optionally substituted moiety linking the two nitrogen atoms of the diamine portion of the salen ligand, where  is selected from the group consisting of a C_3-C_{14} carbocycle, a C_6-C_{10} aryl group, a C_3-C_{14} heterocycle, and a C_5-C_{10} heteroaryl group; or an optionally substituted C_{2-20} aliphatic group, wherein one or more

methylene units are optionally and independently replaced by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-OC(O)N(R^y)-$, $-N(R^y)C(O)O-$, -OC(O)O-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, $-C(=NOR^y)-$ or -N=N-.

[0172] In some embodiments metal complexes having formula **Ia** above, at least one of the phenyl rings comprising the salicylaldehyde-derived portion of the metal complex is independently selected from the group consisting of:



[0173] In some embodiments, a provided Lewis acid comprises a metallo salen compound, conforming to one of formulae **Va** or **Vb**:



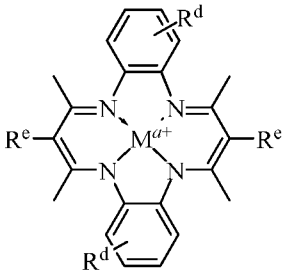
Va or **Vb**

where M, a, R^d, R^{1a}, R^{3a}, $R^{1a'}$, $R^{3a'}$, and , are as defined above and in the classes and subclasses herein.

[0174] In some embodiments of metal complexes having formulae **Va** or **Vb**, each R^{1a} and R^{3a} is, independently, optionally substituted C_1-C_{20} aliphatic.

[0175] In some embodiments, the moiety  comprises an optionally substituted 1,2-phenyl moiety.

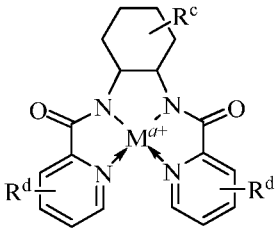
[0176] In some embodiments, Lewis acids included in carbonylation catalysts used in systems and methods described herein comprise metal- tmtaa complexes. In some embodiments, the moiety  has the structure:



where M, *a* and R^d are as defined above and in the classes and subclasses herein, and R^e at each occurrence is independently hydrogen, halogen, -OR, -NR^y_2, -SR^y, -CN, -NO_2, -SO_2R^y, -SOR^y, -$SO_2NR^y_2$; -CNO, -$NR^ySO_2R^y$, -NCO, -N_3, -SiR^y_3; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-

membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur.

[0177] In some embodiments, the moiety  has the structure:



,

where each of M, *a*, R^c and R^d is as defined above and in the classes and subclasses herein.

[0178] In some embodiments, where carbonylation catalysts used in systems and methods described herein include a Lewis acidic metal complex, the metal atom is selected from the periodic table groups 2-13, inclusive. In some embodiments, M is a transition metal selected from the periodic table groups 4, 6, 11, 12 and 13. In some embodiments, M is aluminum, chromium, titanium, indium, gallium, zinc cobalt, or copper. In some embodiments, M is aluminum. In other embodiments, M is chromium.

[0179] In some embodiments, M has an oxidation state of +2. In some embodiments, M is Zn(II), Cu(II), Mn(II), Co(II), Ru(II), Fe(II), Co(II), Rh(II), Ni(II), Pd(II) or Mg(II). In some embodiments M is Zn(II). In some embodiments M is Cu(II).

[0180] In some embodiments, M has an oxidation state of +3. In some embodiments, M is Al(III), Cr(III), Fe(III), Co(III), Ti(III) In(III), Ga(III) or Mn(III). In some embodiments M is Al(III). In some embodiments M is Cr(III).

[0181] In some embodiments, M has an oxidation state of +4. In some embodiments, M is Ti(IV) or Cr(IV).

[0182] In some embodiments, M^1 and M^2 are each independently a metal atom selected from the periodic table groups 2-13, inclusive. In some embodiments, M is a transition metal

selected from the periodic table groups 4, 6, 11, 12 and 13. In some embodiments, M is aluminum, chromium, titanium, indium, gallium, zinc cobalt, or copper. In some embodiments, M is aluminum. In other embodiments, M is chromium. In some embodiments, M^1 and M^2 are the same. In some embodiments, M^1 and M^2 are the same metal, but have different oxidation states. In some embodiments, M^1 and M^2 are different metals.

[0183] In some embodiments, one or more of M^1 and M^2 has an oxidation state of +2. In some embodiments, M^1 is Zn(II), Cu(II), Mn(II), Co(II), Ru(II), Fe(II), Co(II), Rh(II), Ni(II), Pd(II) or Mg(II). In some embodiments M^1 is Zn(II). In some embodiments M^1 is Cu(II). In some embodiments, M^2 is Zn(II), Cu(II), Mn(II), Co(II), Ru(II), Fe(II), Co(II), Rh(II), Ni(II), Pd(II) or Mg(II). In some embodiments M^2 is Zn(II). In some embodiments M^2 is Cu(II).

[0184] In some embodiments, one or more of M^1 and M^2 has an oxidation state of +3. In some embodiments, M^1 is Al(III), Cr(III), Fe(III), Co(III), Ti(III) In(III), Ga(III) or Mn(III). In some embodiments M^1 is Al(III). In some embodiments M^1 is Cr(III). In some embodiments, M^2 is Al(III), Cr(III), Fe(III), Co(III), Ti(III) In(III), Ga(III) or Mn(III). In some embodiments M^2 is Al(III). In some embodiments M^2 is Cr(III).

[0185] In some embodiments, one or more of M^1 and M^2 has an oxidation state of +4. In some embodiments, M^1 is Ti(IV) or Cr(IV). In some embodiments, M^2 is Ti(IV) or Cr(IV).

[0186] In some embodiments, the metal-centered Lewis-acidic component of the carbonylation catalyst includes a dianionic tetradentate ligand. In some embodiments, the dianionic tetradentate ligand is selected from the group consisting of: porphyrin derivatives; salen derivatives; dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives; phthalocyaninate derivatives; and derivatives of the Trost ligand.

[0187] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum porphyrin compound. In some embodiments, the carbonylation

catalyst is $[(TPP)Al(THF)_2][Co(CO)_4]$ where TPP stands for tetraphenylporphyrin and THF stands for tetrahydrofuran.

[0188] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium porphyrin compound.

[0189] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salen compound. In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salophen compound.

[0190] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum salen compound. In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum salophen compound.

[0191] In some embodiments, one or more neutral two electron donors coordinate to M M^1 or M^2 and fill the coordination valence of the metal atom. In some embodiments, the neutral two electron donor is a solvent molecule. In some embodiments, the neutral two electron donor is an ether. In some embodiments, the neutral two electron donor is tetrahydrofuran, diethyl ether, acetonitrile, carbon disulfide, or pyridine. In some embodiments, the neutral two electron donor is tetrahydrofuran . In some embodiments, the neutral two electron donor is an epoxide. In some embodiments, the neutral two electron donor is an ester or a lactone.

[0192] In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum porphyrin compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium porphyrin compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salen compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salophen compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination

with an aluminum salen compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum salophen compound.

Biphasic Carbonylation Catalysts

[0193] In some embodiments, the carbonylation catalyst is biphasic. Thus, in certain variations, the carbonylation reaction product mixture comprises at least two phases, wherein one phase is a catalyst phase and a second phase is a product phase, wherein following the carbonylation reaction, the majority of the carbonylation catalyst is located in the catalyst phase, and the majority of the bPL produced is located in the product phase. For example, in some embodiments, between 50 wt % and 100 wt %, between 60 wt % and 100 wt %, between 70 wt % and 100 wt %, between 80 wt % and 100 wt %, between 90 wt % and 100 wt %, or between 95 wt % and 100 wt % of the carbonylation catalyst is located in the catalyst phase. In some embodiments, between 50 wt % and 100 wt %, between 60 wt % and 100 wt %, between 70 wt % and 100 wt %, between 80 wt % and 100 wt %, between 90 wt % and 100 wt %, or between 95 wt % and 100 wt % of the bPL produced is located in the product phase. In some embodiments, the biphasic carbonylation catalyst is any of the carbonylation catalysts described herein, provided the catalyst is at least partially immiscible with bPL. In other embodiments, the carbonylation catalyst is any of the carbonylation catalysts described herein modified to contain a substituent to make the modified catalyst at least partially immiscible with bPL.

[0194] In some embodiments, the carbonylation catalyst is at least partially immiscible with bPL under certain conditions, but miscible with bPL under other conditions. For example, in some variations, the biphasic catalyst is completely miscible with bPL in the carbonylation product stream at one temperature and at least partially immiscible with bPL in the carbonylation product stream at a lower temperature. In other variations, the biphasic catalyst comprises one or more ionizable functional groups which enable the catalyst to be miscible

with bPL in the carbonylation product stream at one pH, and at least partially immiscible at a different pH. Thus, in some embodiments, the biphasic catalyst is combined with EO and CO at a first pH to produce bPL, wherein the biphasic catalyst is miscible with bPL, and then the pH of the reaction mixture is changed such that the biphasic catalyst is at least partially immiscible with bPL.

Monitoring and Replacing Catalyst

[0195] In one aspect, the production system/production process is configured for continuous carbonylation of an epoxide or lactone feedstock, the process comprising the steps of:

reacting an epoxide or lactone feedstock with carbon monoxide in the presence of a catalyst comprising a Lewis acid and a metal carbonyl in a carbonylation reaction vessel;

measuring one or more parameters selected from the group consisting of:

i) a concentration of the Lewis acid, or a decomposition product thereof, within the carbonylation reaction vessel;

ii) a concentration of the Lewis acid, or a decomposition product thereof, in a product stream downstream from the carbonylation reaction vessel;

iii) a concentration of the metal carbonyl, or a decomposition product thereof, within the carbonylation reaction vessel;

iv) a concentration of the metal carbonyl, or a decomposition product thereof, in a product stream downstream from the carbonylation reaction vessel; and

v) a rate of the carbonylation reaction;

comparing the measured value of the one or more parameters to predetermined reference values for the one or more parameters; and

where the measured value of any one of parameters i), iii), or v) is less than the reference value, or where the measured value of any one of parameters ii) or iv) is greater than the

reference value, introducing to the carbonylation reaction vessel a catalyst replacement component which is different from the catalyst and comprises a species selected from the group consisting of the Lewis acid, a precursor to the Lewis acid, the metal carbonyl, and a precursor to the metal carbonyl.

[0196] In some embodiments, one of the one or more parameters measured is the concentration of the Lewis acid, or a decomposition product thereof, within the carbonylation reaction vessel. In some embodiments, the concentration of the Lewis acid within the carbonylation reaction vessel is measured. In some embodiments, the concentration of a decomposition product of the Lewis acid within the carbonylation reaction vessel is measured.

[0197] In some embodiments, one of the one or more parameters measured is the concentration of the metal carbonyl, or a decomposition product thereof, within the carbonylation reaction vessel. In some embodiments, the concentration of the metal carbonyl within the carbonylation reaction vessel is measured. In some embodiments, the concentration of a decomposition product of the metal carbonyl within the carbonylation reaction vessel is measured.

[0198] In some embodiments, one of the one or more parameters measured is the concentration of the Lewis acid, or a decomposition product thereof, in the product stream downstream from the carbonylation reaction vessel. In some embodiments, the concentration of the Lewis acid in the product stream downstream from the carbonylation reaction vessel is measured. In some embodiments, the concentration of a decomposition product of the Lewis acid in the product stream downstream from the carbonylation reaction vessel is measured.

[0199] In some embodiments, one of the one or more parameters measured is the concentration of the metal carbonyl, or a decomposition product thereof, in the product stream downstream from the carbonylation reaction vessel. In some embodiments, the concentration of the metal carbonyl in the product stream downstream from the carbonylation reaction vessel

is measured. In some embodiments, the concentration of a decomposition product of the metal carbonyl in the product stream downstream from the carbonylation reaction vessel is measured.

[0200] In some embodiments, one of the one or more parameters measured is the rate of the carbonylation reaction. In some embodiments, the rate of the carbonylation reaction is measured by the change in concentration of a carbonylation product in the carbonylation reaction vessel over time. In some embodiments, the rate of the carbonylation reaction is measured by the change in concentration of a carbonylation product in the product stream downstream from the carbonylation reaction vessel over time. In some embodiments, the carbonylation product is a beta-propiolactone. In some embodiments, the carbonylation product is beta-propiolactone (bPL). In some embodiments, the carbonylation product is a succinic anhydride. In some embodiments the carbonylation product is succinic anhydride (SA).

[0201] In some embodiments, the product stream is separated from the carbonylation reaction vessel by a nanofiltration membrane. In some embodiments, the nanofiltration membrane is selected based on its ability to retain solutes having a molecular weight greater than the molecular weight of the epoxide or lactone carbonylation products, but less than the molecular weights of either the Lewis acid or the metal carbonyl. In some embodiments, the nanofiltration membrane is designed to retain solutes having a molecular weight greater than the molecular weight of the epoxide or lactone carbonylation products, but less than the molecular weights of either the Lewis acid or the metal carbonyl.

[0202] In some embodiments, the catalyst replacement component comprises the Lewis acid, or a precursor to the Lewis acid. In some embodiments, the catalyst replacement component comprises the Lewis acid. In some embodiments, the catalyst replacement component comprises a precursor to the Lewis acid.

[0203] In some embodiments, the catalyst replacement component comprises the metal carbonyl, or a precursor to the metal carbonyl. In some embodiments, the catalyst replacement component comprises the metal carbonyl. In some embodiments, the catalyst replacement component comprises a precursor to the metal carbonyl.

[0204] In some embodiments, where more than one catalyst replacement component is added, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel separately. In some embodiments, where more than one catalyst replacement component is added, all of the one or more catalyst replacement components are added to the carbonylation reaction vessel together.

[0205] In some embodiments, each of the one or more catalyst replacement components is added individually to the carbonylation reaction vessel without solvent, as a solution in an organic solvent, or as a slurry. In some embodiments, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel without solvent. In some embodiments, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel as a solution in an organic solvent. In some embodiments, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel as a slurry.

[0206] In certain embodiments, where more than one catalyst replacement component are added, each catalyst replacement component is dissolved in solution, and the solutions are combined enroute to the vessel, e.g., by using a mixing tee or flowing the combined solutions through a static mixer.

[0207] In certain embodiments, fresh catalyst may also be added to the reaction vessel at the same or different times as the one or more catalyst replacement components.

[0208] In certain embodiments, the catalyst replacement components are added under an atmosphere comprising CO. In certain embodiments, the CO is present at a pressure from

about 1 atmosphere to about 400 atmospheres. In certain embodiments, the catalyst replacement components are added under an atmosphere comprising CO at a pressure between about 1 atmosphere and about 100 atmospheres, or between about 1 atmosphere and about 50 atmospheres, or between about 10 atmospheres and about 20 atmospheres, or between about 5 atmospheres and about 10 atmospheres, or between about 1 atmosphere and about 5 atmospheres.

[0209] In some embodiments, the amount of a given catalyst replacement component added to the carbonylation reaction vessel is proportional to one of the parameters being measured in step (a). In some embodiments, the amount of a given catalyst replacement component is directly proportional to changes in the concentration of the parameter measured in the product stream downstream from the carbonylation reaction vessel.

[0210] In some embodiments, if the concentration of the Lewis acid, or a decomposition product thereof, measured in step (a) is increased in the product stream downstream from the carbonylation reaction vessel, an amount of Lewis acid that is proportional to the increase in the concentration of Lewis acid, or a decomposition product thereof, measured in step (a) is added to the carbonylation reaction vessel. In some embodiments, if the concentration of the Lewis acid, or a decomposition product thereof, measured in step (a) is decreased within the carbonylation reaction vessel, an amount of Lewis acid, or a precursor to the Lewis acid, that is proportional to the decrease in the concentration of Lewis acid, or a decomposition product thereof, measured in step (a) is added to the carbonylation reaction vessel. For example, if the concentration of the Lewis acid has decreased by 5%, an amount of the Lewis acid or precursor to the Lewis acid that is equivalent to about 5% of the amount of the Lewis acid initially charged into the carbonylation reaction vessel is added.

[0211] In some embodiments, if the rate of the carbonylation reaction, measured in step (a) is decreased, an amount of Lewis acid, or a precursor to the Lewis acid, that is proportional to the decrease in the rate of the carbonylation reaction is added to the carbonylation reaction vessel. In some embodiments, if the rate of the carbonylation reaction measured in step (a) is decreased, an amount of the metal carbonyl or a precursor to the metal carbonyl that is proportional to the decrease in the rate of the carbonylation reaction is added to the carbonylation reaction vessel. For example, if the rate of the carbonylation reaction has decreased by 5%, an amount of Lewis acid, precursor to the Lewis acid, metal carbonyl, or precursor to the metal carbonyl that is equivalent to about 5% of the amount of the Lewis acid or metal carbonyl initially charged into the carbonylation reaction vessel is added.

[0212] In some embodiments, if the concentration of the metal carbonyl, measured in step (a) is increased in the product stream downstream from the carbonylation reaction vessel, an amount of metal carbonyl, or a precursor to the metal carbonyl that is proportional to the increase in the amount of metal carbonyl measured in step (a) is added to the carbonylation reaction vessel. In some embodiments, if the concentration of the metal carbonyl, or a decomposition product thereof, measured in step (a) is decreased within the carbonylation reaction vessel, an amount of metal carbonyl, or a precursor to the metal carbonyl, that is proportional to the decrease in the amount of metal carbonyl, or a decomposition product thereof, measured in step (a) is added to the carbonylation reaction vessel. For example, if the concentration of the metal carbonyl has decreased by 5%, an amount of the metal carbonyl or precursor to the metal carbonyl that is equivalent to about 5% of the amount of the metal carbonyl initially charged into the carbonylation reaction vessel is added.

[0213] FIG. **14** includes carbonylation catalyst source 1403 that can feed fresh carbonylation catalyst in carbonylation catalyst stream 1407 to carbonylation reaction system inlet 1409. Carbonylation catalyst can arrive to the carbonylation catalyst source as either

solids (perhaps blanketed under CO or a suitable inert gas) or in solution of solvent such as hexane or THF. If solid catalysts, the solids can be unpacked and loaded into one or more hoppers under inert conditions (for example, CO or inert gas). The solids from the one or more hoppers can be metered into a suitable solvent before pumping. In some embodiments, the solid catalyst (or liquid catalyst) or catalyst precursors can be dispensed from a shipping vessel/container into an intermediate inert vessel to be mixed with solvent and then pumped. In some embodiments, the catalyst preparation system and connections are selected such that the catalyst/precursors are not exposed to the atmosphere. Carbonylation catalyst solutions can be suitable for direct pumping to the carbonylation reaction system. In some embodiments, the carbonylation catalyst feed is pumped under CO pressure to help ensure stability of the catalyst. Furthermore, carbonylation catalyst source and feed can be cooled below ambient temperature to ensure stability. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at between about 0.01 to 50 kg/hr, between about 0.01 to 40 kg/hr, between about 0.01 to 30 kg/hr, between about 0.01 to 20 kg/hr, between about 0.01 to 10 kg/hr, between about 0.2-5 kg/hr, between about 0.5-4 kg/hr, between about 1-3 kg/hr, between about 1-2 kg/hr, or about 1.4 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at between about 0.0001-10 kmol/hr, between about 0.0001-1 kmol/hr, between about 0.0001-0.1 kmol/hr, between about 0.0001-0.01 kmol/hr, between about 0.0005-0.001 kmol/hr, between about 0.0005-0.005 kmol/hr, or about 0.001 kmol/hr, or about 0.01 kmol/hr, or about 0.1 kmol/hr. In some embodiments, the carbonylation catalyst can be in a solvent such as THF so that the mass fraction of carbonylation catalyst in the stream from the carbonylation catalyst source can be between about 0.001-0.1, about 0.005-0.05, about 0.01-0.05, or about 0.02. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at a

temperature between about 10-30°C, between about 15-25°C, or about 20°C. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Carbon Monoxide Source

[0214] Carbon monoxide is fed into the β-propiolactone production system/production process at an amount sufficient to carbonylate ethylene oxide to produce β-propiolactone. In some variations, this may be achieved performing the carbonylation reaction under a superatmospheric pressure of carbon monoxide. In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure in the range from about 50 psi (350 kPa) to about 5000 psi (35 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure from about 50 psi (350 kPa) to about 1000 psi (7 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure from about 50 psi (350 kPa) to about 500 psi (3.5 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure from about 100 psi (700 kPa) to about 400 psi (2.8 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure of about 200 psi (1.4 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process under an atmosphere having a partial pressure of CO of about 200 psi (1.4 MPa). The superatmospheric pressure of carbon monoxide may be provided in the form of pure carbon monoxide, or by providing a gas mixture containing carbon monoxide. In certain embodiments, the carbon monoxide may be provided in the form of substantially pure carbon monoxide. In other embodiments, the carbon monoxide may be provided in the form of

carbon monoxide mixed with one or more inert gases. In other embodiments, the carbon monoxide may be provided in the form of a mixture of carbon monoxide and hydrogen. In certain embodiments, the carbon monoxide may be provided in the form of a carbon monoxide-containing industrial process gas such as syngas, coal gas, wood gas, or the like.

[0215] FIG. **14** includes carbon monoxide source **1411** that can feed carbon monoxide to carbonylation reaction system inlet **1409**. In some embodiments, the carbon monoxide source that supplies carbon monoxide to the carbonylation reaction system can include fresh carbon monoxide source **1401** (i.e., main CO feed) and recycled carbon monoxide stream **1410** from the carbonylation reaction system. In some embodiments, the carbon monoxide source can be only the fresh carbon monoxide source. In some embodiments, the carbon monoxide source can be only the recycled carbon monoxide. In some embodiments, fresh carbon monoxide stream **1405** and/or the recycled carbon monoxide streams can be fed into carbon monoxide compressor **1401A** prior to the resultant stream from the carbon monoxide compressor (i.e., reactor carbon monoxide inlet stream) being fed into the carbonylation reaction system. In some embodiments, resultant stream from the carbon monoxide compressor **1411** (i.e., reaction system carbon monoxide inlet stream) can be the carbon monoxide source. The carbon monoxide source can be compressed to the pressure at or above the carbonylation reaction system pressure and then fed to the carbonylation system. In some embodiments, the fresh carbon monoxide source (i.e., main CO feed) and the recycled carbon monoxide can be compressed in separate compressors. One reason recycled carbon monoxide can be compressed separately from the fresh carbon monoxide feed (i.e., main CO feed) to reaction system pressure is to avoid contamination of the main compressor (i.e., fresh feed compressor) with hazardous components such as ethylene oxide and bPL that may be present in the carbon monoxide recycle stream. Some of these potentially hazardous components may be removed from the compressor as partially liquefied components as waste. In some embodiments, these

potentially hazardous components can also be recycled to the carbonylation reaction system. In some embodiments, the compressed carbon monoxide from both compressors can be fed to the carbonylation reaction system as the reaction system carbon monoxide inlet stream.

[0216] In some embodiments, the fresh carbon monoxide source can provide at least about 1000 kg/hr CO, at least about 1200 kg/hr CO, at least about 1400 kg/hr CO, at least about 1500 kg/hr CO, at least about 1600 kg/hr CO, at least about 2000 kg/hr CO, at least about 4000 kg/hr CO, at least about 5000 kg/hr CO, at least about 10000 kg/hr CO, at least about 12000 kg/hr CO, at least about 14000 kg/hr CO, at least about 15000 kg/hr CO, or at least about 16000 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide at least about 30 kmol/hr CO, at least about 40 kmol/hr CO, at least about 50 kmol/hr CO, at least about 55 kmol/hr CO, or at least about 60 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide about 1000 kg/hr CO to about 16000 kg/hr CO, about 1200 kg/hr CO to about 16000 kg/hr CO, about 1400 kg/hr CO to about 16000 kg/hr CO, about 1500 kg/hr CO to about 16000 kg/hr CO, about 1600 kg/hr CO to about 16000 kg/hr CO, about 2000 kg/hr CO to about 16000 kg/hr CO, about 4000 kg/hr CO to about 16000 kg/hr CO, about 6000 kg/hr CO to about 16000 kg/hr CO, about 1000 kg/hr CO to about 16000 kg/hr CO, or about 1400 kg/hr CO to about 16000 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide about 1000 kg/hr CO, about 1200 kg/hr CO, about 1400 kg/hr CO, about 1500 kg/hr CO, about 1600 kg/hr CO, about 1800 kg/hr CO, about 2000 kg/hr CO, about 2400 kg/hr CO, about 2600 kg/hr CO, about 2800 kg/hr CO, about 3000 kg/hr CO, about 3200 kg/hr CO, about 4000 kg/hr CO, about 6000 kg/hr CO, about 8000 kg/hr CO, about 10000 kg/hr CO, about 12000 kg/hr CO, about 14000 kg/hr CO, or about 16000 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide at least about 30 kmol/hr CO, at least about 40 kmol/hr CO, at least about 50 kmol/hr CO, at least about 55 kmol/hr CO, at least about 60 kmol/hr CO, at least about 100 kmol/hr CO, at least about 150 kmol/hr CO, at least

about 200 kmol/hr CO, at least about 250 kmol/hr CO, at least about 300 kg/hr CO, at least about 350 kmol/hr CO, at least about 400 kmol/hr CO, at least about 500 kmol/hr CO, at least about 550 kmol/hr CO, or at least about 600 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide about 30 kmol/hr CO to about 60 kmol/hr CO, about 40 kmol/hr CO to about 60 kmol/hr CO, about 50 kmol/hr CO to about 60 kmol/hr CO, about 30 kmol/hr CO to about 600 kmol/hr CO, about 40 kmol/hr CO to about 600 kmol/hr CO, about 50 kmol/hr CO to about 600 kmol/hr CO, about 55 kmol/hr CO to about 600 kmol/hr CO, about 100 kmol/hr CO to about 600 kmol/hr CO, about 200 kg/hr CO to about 600 kmol/hr CO, about 300 kmol/hr CO to about 600 kmol/hr CO, about 400 kmol/hr CO to about 600 kmol/hr CO, about 500 kmol/hr CO to about 600 kmol/hr CO, about 525 kmol/hr CO to about 600 kmol/hr CO, about 550 kg/hr CO to about 600 kmol/hr CO. In some embodiments, the fresh carbon monoxide from the fresh carbon monoxide source may have some impurities and thus may require additional purification steps such as adsorption. In some embodiments, the flow rate from the fresh carbon monoxide source is set to about the stoichiometric value for the carbonylation reaction, to about 5% higher than the stoichiometric value, to about 10% higher than the stoichiometric value, to about 15% higher than the stoichiometric value, or to about 20% higher than the stoichiometric value.

[0217] In some embodiments, the recycled carbon monoxide from the carbonylation reaction system can provide at least about 100 kg/hr CO, at least about 150 kg/hr CO, at least about 200 kg/hr CO, at least about 255 kg/hr CO, at least about 300 kg/hr CO, at least about 350 kg/hr CO, at least about 500 kg/hr CO, at least about 600 kg/hr CO, at least about 800 kg/hr CO, at least about 1000 kg/hr CO, at least about 1250 kg/hr CO, at least about 1500 kg/hr CO, at least about 1750 kg/hr CO, at least about 2000 kg/hr CO, at least about 2500 kg/hr CO, at least about 3000 kg/hr CO, or at least about 3500 kg/hr CO. In some embodiments, the recycled carbon monoxide from the carbonylation reaction system can provide from about 100

kg/hr CO to about 350 kg/hr CO, about 150 kg/hr CO to about 350 kg/hr CO, about 200 kg/hr CO to about 350 kg/hr CO, about 255 kg/hr CO to about 350 kg/hr CO, about 300 kg/hr CO to about 350 kg/hr CO, from about 100 kg/hr CO to about 3500 kg/hr CO, about 150 kg/hr CO to about 3500 kg/hr CO, about 200 kg/hr CO to about 3500 kg/hr CO, about 255 kg/hr CO to about 3500 kg/hr CO, about 300 kg/hr CO to about 3500 kg/hr CO, about 350 kg/hr CO to about 3500 kg/hr CO, about 1000 kg/hr CO to about 3500 kg/hr CO, about 1500 kg/hr CO to about 3500 kg/hr CO, about 2000 kg/hr CO to about 3500 kg/hr CO, about 2550 kg/hr CO to about 3500 kg/hr CO, about 3000 kg/hr CO to about 3500 kg/hr CO. In some embodiments, the recycled carbon monoxide from the carbonylation reaction system can provide about 100 kg/hr CO, about 150 kg/hr CO, about 200 kg/hr CO, about 255 kg/hr CO, about 300 kg/hr CO, about 350 kg/hr CO, about 500 kg/hr CO, about 750 kg/hr CO, about 1000 kg/hr CO, about 1250 kg/hr CO, about 1500 kg/hr CO, about 2000 kg/hr CO, about 2500 kg/hr CO, about 3000 kg/hr CO, or about 3500 kg/hr CO. In some embodiments, the recycled carbon monoxide source can provide at least about 3 kmol/hr CO, at least about 5 kmol/hr CO, at least about 7 kmol/hr CO, at least about 9 kmol/hr CO, at least about 10 kmol/hr CO, at least about 15 kmol /hr CO, at least 50 kmol /hr CO, at least 100 kmol /hr CO, or at least 150 kmol /hr CO. In some embodiments, the mass fraction of CO in the recycled carbon monoxide stream can be at least about 0.70, at least about 0.75, at least about 0.8, or at least about 0.85. In some embodiments, the mole fraction of CO in the recycled carbon monoxide stream can be at least about 0.70, at least about 0.75, at least about 0.8, at least about 0.85, at least about 0.896, at least about 0.9, or at least about 0.95. In some embodiments, the mole fraction of CO in the recycled carbon monoxide stream can be 0.70 to 1.0, 0.75 to 1.0, 0.8 to 1.0, 0.85 to 1.0, 0.896 to 1.0, 0.9 to 1.0, or 0.95 to 1.0. The recycled carbon monoxide stream from the carbonylation reaction system can also include unreacted ethylene oxide (in about at most 10 kg/hr, at most 15 kg/hr, at most 20 kg/hr, at most 25 kg/hr, at most 50 kg/hr, at most 75 kg/hr, at most 100 kg/hr, at most 150

kg/hr, at most 200 kg/hr, or at most 250 kg/hr or a mass fraction of between about 0.05-0.075, about 0.055-0.07, about 0.06-0.07, about at most 0.065, about at most 0.07, or about at most 0.075), secondary reaction product acetaldehyde (in about at most 0.5 kg/hr, at most about 1 kg/hr, at most about 1.3 kg/hr, at most about 2 kg/hr, at most about 4 kg/hr, at most about 6 kg/hr, at most about 10 kg/hr, at most about 13 kg/hr or a mass fraction of about 0.001-0.009, about 0.003-0.005, or about most 0.004, about at most 0.005, or at most about 0.009), bPL (in about at most about 0.005 kg/hr, at most about 0.01 kg/hr, at most about 0.015 kg/hr, about at most about 0.019 kg/hr, at most about 0.05 kg/hr, at most about 0.1 kg/hr, at most about 0.15 kg/hr, or about at most about 0.19 kg/hr), and the remainder solvent (e.g., THF).

[0218] In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at least about 1000 kg/hr, at least about 1250 kg/hr, at least about 1500 kg/hr, at least about 1600 kg/hr, at least about 1655 kg/hr, at least about 1700 kg/hr, at least about 4000 kg/hr, at least about 5000 kg/hr, at least about 700 kg/hr, at least about 8500 kg/hr, at least about 10000 kg/hr, at least about 12500 kg/hr, at least about 15000 kg/hr, at least about 16000 kg/hr, at least about 16550 kg/hr, or at least about 17000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at about 1000 kg/hr to about 1700 kg/hr, about 1250 kg/hr to about 1700 kg/hr, about 1500 kg/hr to about 1700 kg/hr, about 1600 kg/hr to about 1700 kg/hr, about 1655 kg/hr to about 1700 kg/hr, 1000 kg/hr to about 17000 kg/hr, about 1250 kg/hr to about 17000 kg/hr, about 1500 kg/hr to about 17000 kg/hr, about 1600 kg/hr to about 17000 kg/hr, about 1655 kg/hr to about 17000 kg/hr, about 1700 kg/hr to about 17000 kg/hr, at about 2000 kg/hr to about 17000 kg/hr, about 3000 kg/hr to about 17000 kg/hr, about 4000 kg/hr to about 17000 kg/hr, about 6000 kg/hr to about 17000 kg/hr, about 8000 kg/hr to about 17000 kg/hr, about 1200 kg/hr to about 17000 kg/hr, about 1400 kg/hr to about 17000 kg/hr, about 1500 kg/hr to about 17000 kg/hr, or about 1600 kg/hr to about 17000 kg/hr. In some

embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at about 1000 kg/hr, about 1250 kg/hr, about 1500 kg/hr, about 1600 kg/hr, about 1655 kg/hr, about 1700 kg/hr, about 2000 kg/hr, about 1900 kg/hr, about 2500 kg/hr, about 3000 kg/hr, about 4000 kg/hr, about 6000 kg/hr, about 8000 kg/hr, about 10000 kg/hr, about 12000 kg/hr, about 13000 kg/hr, about 14000 kg/hr, about 15000 kg/hr, about 16000 kg/hr, or about 17000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at least about 35 kmol/hr, at least about 45 kmol/hr, at least about 50 kmol/hr, at least about 55 kmol/hr, or at least about 59 kmol/hr. As previously discussed, in some embodiments, the carbon monoxide source can include some recycled carbon monoxide from the carbonylation reaction system. Accordingly, in some embodiments, the inlet to the carbonylation reaction system can also receive ethylene oxide (in about 5-300 kg/hr, about 10-200 kg/hr, about 10-100 kg/hr, about 10-50 kg/hr, about 10-30 kg/hr, about 10-20 kg/hr, or at most about 15 kg/hr, at most about 50 kg/hr, at most about 100 kg/hr, at most about 150 kg/hr, at most about 200 kg/hr, at most about 300 kg/hr, or a mass fraction of about 0.001-0.05, about 0.005-0.02, or at most about 0.009, at most about 0.02, or at most about 0.05), acetaldehyde (in about 0.25-15 kg/hr, about 0.5-12.5 kg/hr, about 0.25-10 kg/hr, about 0.5-5 kg/hr, about 0.25-1.5 kg/hr, about 0.5-1.25 kg/hr, or at most about 0.9 kg/hr, at most about 1.5 kg/hr, at most about 3 kg/hr, at most about 6 kg/hr, at most about 12 kg/hr, at most about 15 kg/hr, or a mass fraction of about 0.001-0.05, about 0.005-0.02, or at most about 0.009, at most about 0.02, or at most about 0.05), and the remainder solvent from the carbon monoxide source. In some embodiments, the mass fraction of CO from the carbon monoxide source can be at least about 0.9, at least about 0.95, at least about 0.985, or at least about 0.99. In some embodiments, the mole fraction of CO from the carbon monoxide source can be at least about 0.9, at least about 0.95, at least about 0.98, at least about 0.99, or at least about 0.995. In some embodiments, the mole fraction of CO from

the carbon monoxide source can be 0.9 to 1.0, 0.95 to 1.0, 0.98 to 1.0, 0.99 to 1.0, or 0.995 to 1.0.

[0219] In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at a temperature between about 10-170°C, between about 30-70°C, between about 40-60°C, between about 45-55°C, or about 50°C. In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Solvent Source

[0220] The solvent may be selected from any solvents described herein, and mixtures of such solvents. In some variations, the solvent is an organic solvent. In certain variations, the solvent is an aprotic solvent.

[0221] In some embodiments, the solvent includes dimethylformamide, N-methyl pyrrolidone, tetrahydrofuran, toluene, xylene, diethyl ether, methyl-tert-butyl ether, acetone, methylethyl ketone, methyl-iso-butyl ketone, butyl acetate, ethyl acetate, dichloromethane, and hexane, and mixtures of any two or more of these. In general polar aprotic solvents or hydrocarbons are suitable for this step.

[0222] Additionally, in one variation, β-lactone may be utilized as a co-solvent. In other variations, the solvent may include ethers, hydrocarbons and non protic polar solvents. In some embodiments, the solvent includes tetrahydrofuran ("THF"), sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, dimethoxy ethane, acetone, and methylethyl ketone. In other embodiments, the solvent includes tetrahydrofuran, tetrahydropyran, 2,5-dimethyl

tetrahydrofuran, sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, propyl acetate, butyl acetate, 2-butanone, cyclohexanone, toluene, difluorobenzene, dimethoxy ethane, acetone, and methylethyl ketone. In certain variations, the solvent is a polar donating solvent. In one variation, the solvent is THF.

[0223] In some embodiments, the catalyst and/or solvent stream is recycled to the feed stream or to the carbonylation reaction system. In some embodiments, the portion of the solvent and/or catalyst from the reaction product stream recycled to the carbonylation reactor or feed stream ranges from about 0% to about 100%. In some embodiments, the portion of the solvent and/or catalyst from the reaction product stream recycled to the carbonylation reactor or feed stream is about 100%, about 90%, about 80%, about 70%, about 60%, about 50%, about 40%, about 30%, about 20%, about 10%, or about 0%. In some embodiments, a different percentage of the catalyst, as compared to the solvent is recycled, i.e., the proportions of either the catalyst or solvent component do not need to be equal.

[0224] Referring again to the exemplary system depicted in FIG. **14**, in some embodiments, solvent feed 1424 can supply solvent to the carbonylation reaction system inlet 1409. Solvent can be fed to the carbonylation reaction system suing a pump. In addition, the solvent streams, sources, storage tanks, etc, can be maintained under an inert or CO atmosphere. In some embodiments, the solvent feed that supplies solvent to the carbonylation reaction system can include solvent 1408 from fresh solvent source 1404, recycled solvent 1423 from the BPL purification system, and/or solvent in recycled carbonylation catalyst stream 1412 from the carbonylation catalyst isolation system. In some embodiments, the recycled solvent from the BPL purification system can be stored in a make-up solvent reservoir. In some embodiments,

the solvent feed that supplies solvent to the carbonylation reaction system can include solvent from the make-up solvent reservoir. In some embodiments, solvent can be purged from the system. In some embodiments, the purged solvent can be solvent from the recycled solvent of the BPL purification system. In some embodiments, solvent from the fresh solvent source is also stored into the make-up solvent reservoir to dilute the recycled solvent from the BPL purification system with fresh solvent. In some embodiments, fresh solvent is fed from the fresh solvent source to the make-up solvent reservoir prior to entering the carbonylation reaction system. In some embodiments, solvent from the fresh solvent source, the BPL purification system, and the carbonylation catalyst isolation system can be purified by operations such as adsorption to remove oxygen and water that can inhibit the carbonylation catalyst. In some embodiments, the amount of oxygen and/or water in all streams entering the carbonylation reaction system is less than about 500 ppm, less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, less than about 20 ppm, less than about 10 ppm, less than about 5 ppm, less than about 2 ppm, or less than about 1 ppm.

[0225] In some embodiments, the fresh solvent source can provide at least about 50 kg/hr solvent, at least about 100 kg/hr solvent, at least about 150 kg/hr solvent, at least about 188 kg/hr solvent, at least about 200 kg/hr solvent, at least about 250 kg/hr solvent, at least about 500 kg/hr solvent, at least about 1000 kg/hr solvent, at least about 1500 kg/hr solvent, at least about 1880 kg/hr solvent, at least about 2000 kg/hr solvent, or at least about 2500 kg/hr solvent. In some embodiments, the fresh solvent source can provide about 50 kg/hr to about 250 kg/hr solvent, about 100 kg/hr to about 250 kg/hr solvent, about 150 kg/hr to about 250 kg/hr solvent, about 188 kg/hr to about 250 kg/hr solvent, about 200 kg/hr to about 250 kg/hr solvent, about 50 kg/hr to about 2500 kg/hr solvent, about 100 kg/hr to about 2500 kg/hr solvent, about 150 kg/hr to about 2500 kg/hr solvent, about 188 kg/hr to about 2500 kg/hr solvent, about 200 kg/hr to about 2500 kg/hr solvent, about 250 kg/hr to about 2500 kg/hr solvent, about 500 kg/hr to

about 2500 kg/hr solvent, about 1000 kg/hr to about 2500 kg/hr solvent, about 1500 kg/hr to about 2500 kg/hr solvent, about 1880 kg/hr to about 2500 kg/hr solvent, about 2000 kg/hr to about 2500 kg/hr solvent, or about 2250 kg/hr to about 2500 kg/hr solvent. In some embodiments, the fresh solvent source can provide about 50 kg/hr solvent, about 100 kg/hr solvent, about 150 kg/hr solvent, about 188 kg/hr solvent, about 200 kg/hr solvent, about 250 kg/hr solvent, about 500 kg/hr solvent, about 1000 kg/hr solvent, about 1500 kg/hr solvent, about 1880 kg/hr solvent, about 2000 kg/hr solvent, or about 2500 kg/hr solvent. In some embodiments, the fresh solvent source can provide at least about 1 kmol/hr solvent, at least about 2 kmol/hr solvent, at least about 2.6 kmol/hr solvent, at least about 3 kmol/hr solvent, at least about 50 kmol/hr solvent, at least about 100 kmol/hr solvent, at least about 150 kmol/hr solvent, at least about 250 kmol/hr solvent, at least about 400 kmol/hr solvent, or at least about 500 kmol/hr solvent.

[0226] In some embodiments, the recycled solvent from the BPL purification system can provide at least about 8000 kg/hr solvent, at least about 9000 kg/hr solvent, at least about 10000 kg/hr solvent, at least about 10444 kg/hr solvent, at least about 12000 kg/hr solvent, at least about 80000 kg/hr solvent, at least about 90000 kg/hr solvent, at least about 100000 kg/hr solvent, at least about 104440 kg/hr solvent, or at least about 120000 kg/hr solvent. In some embodiments, the recycled solvent from the BPL purification system can provide between about 8000 kg/hr to about 12000 kg/hr solvent, between about 9000 kg/hr to about 12000 kg/hr solvent, between about 10000 kg/hr to about 12000 kg/hr solvent, between about 10444 kg/hr to about 12000 kg/hr solvent, about 8000 kg/hr to about 120000 kg/hr solvent, between about 9000 kg/hr to about 120000 kg/hr solvent, between about 10000 kg/hr to about 120000 kg/hr solvent, between about 10444 kg/hr to about 120000 kg/hr solvent, between about 12000 kg/hr to about 120000 kg/hr solvent, about 40000 kg/hr to about 120000 kg/hr solvent, about 60000 kg/hr to about 120000 kg/hr solvent, about 80000 kg/hr to about 120000 kg/hr solvent, between

about 90000 kg/hr to about 120000 kg/hr solvent, between about 100000 kg/hr to about 120000 kg/hr solvent, between about 104440 kg/hr to about 120000 kg/hr solvent, or between about 120000 kg/hr to about 120000 kg/hr solvent. In some embodiments, the recycled solvent from the BPL purification system can provide about 8000 kg/hr solvent, about 9000 kg/hr solvent, about 10000 kg/hr solvent, about 10444 kg/hr solvent, or about 12000 kg/hr solvent. In some embodiments, the recycled solvent from the BPL purification system can provide at least about 100 kmol/hr solvent, at least about 120 kmol/hr solvent, at least about 140 kmol/hr solvent, at least about 145 kmol/hr solvent, at least about 150 kmol/hr solvent, at least 250 kmol/hr solvent, at least 350 kmol/hr solvent, or at least 500 kmol/hr solvent. In some embodiments, the mass fraction of solvent in the recycled solvent stream can be at least about 0.85, at least about 0.90, at least about 0.95, or at least about 0.995. In some embodiments, the mole fraction of solvent in the recycled solvent stream can be at least about 0.85, at least about 0.90, at least about 0.95, at least about 0.98, at least about 0.99, or at least about 0.993. In some embodiments, the mole fraction of solvent in the recycled solvent stream can be 0.85 to 1.0, 0.90 to 1.0, 0.95 to 1.0, 0.98 to 1.0, 0.99 to 1.0, or 0.993 to 1.0. In some embodiments, the mole fraction of solvent in the recycled solvent stream can be about 0.85, about 0.90, about 0.95, about 0.98, about 0.99, or about 0.993. The recycled solvent stream from the BPL purification system can also include unreacted carbon monoxide (in about at most 0.001 kg/hr, at most about 0.0025 kg/hr, at most about 0.005 kg/hr, at most about 0.01 kg/hr, at most 0.02 kg/hr, at most about 0.025 kg/hr, at most about 0.05 kg/hr, or at most about 0.01 kg/hr or between 0 and 0.005 kg/hr, or between 0 and 0.05 kg/hr) unreacted ethylene oxide (in about at most about 10 kg/hr, at most about 20 kg/hr, at most about 30 kg/hr, at most about 33 kg/hr, at most about 50 kg/hr, at most about 100 kg/hr, at most about 200 kg/hr, or at most about 330 kg/hr, or a mass fraction of between about 0.001-0.005, about 0.02-0.004, or at most about 0.003, at most about 0.004, or at most about 0.005), secondary reaction product acetaldehyde

(in about at most 3 kg/hr, at most about 5 kg/hr, at most about 8.2 kg/hr, at most about 10 kg/hr, at most about 15 kg/hr, at most 30 kg/hr, at most about 50 kg/hr, or at most about 82 kg/hr or a mass fraction of at most about 0.001, or between 0 and 8.2 kg/hr), and bPL (in at most about 2 kg/hr, at most about 3 kg/hr, at most about 5 kg/hr, at most about 7 kg/hr, at most about 10 kg/hr, at most about 25 kg/hr, at most about 50 kg/hr, or at most about 70 kg/hr or a mass fraction of at most about 0.001, or between 0 and 7 kg/hr, or between 0 and 70 kg/hr).

[0227] In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 1000 kg/hr solvent, at least about 1500 kg/hr solvent, at least about 1700 kg/hr solvent, at least about 1840 kg/hr solvent, at least about 2000 kg/hr solvent, at least about 5000 kg/hr solvent, at least about 10000 kg/hr solvent, at least about 15000 kg/hr solvent, at least about 17000 kg/hr solvent, at least about 18400 kg/hr solvent, or at least about 20000 kg/hr solvent. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide about 1000 kg/hr to about 2000 kg/hr solvent, about 1500 kg/hr to about 2000 kg/hr solvent, about 1700 kg/hr to about 2000 kg/hr solvent, about 1840 kg/hr to about 2000 kg/hr solvent, about 1000 kg/hr to about 20000 kg/hr solvent, about 1500 kg/hr to about 20000 kg/hr solvent, about 1700 kg/hr to about 20000 kg/hr solvent, about 1840 kg/hr to about 20000 kg/hr solvent, about 2000 kg/hr to about 20000 kg/hr solvent, about 5000 kg/hr to about 20000 kg/hr solvent, about 7500 kg/hr to about 20000 kg/hr solvent, about 12500 kg/hr to about 20000 kg/hr solvent, about 15000 kg/hr to about 20000 kg/hr solvent, or about 17500 kg/hr to about 20000 kg/hr solvent. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide about 1000 kg/hr solvent, about 1500 kg/hr solvent, about 1700 kg/hr solvent, about 1840 kg/hr solvent, about 2000 kg/hr solvent, about 2500 kg/hr solvent, about 3000 kg/hr solvent, about 5000 kg/hr solvent, about 7000 kg/hr solvent, about 10000 kg/hr solvent, about 12500 kg/hr solvent, about 15000 kg/hr solvent, or

about 20000 kg/hr solvent. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 10 kmol/hr solvent, at least about 15 kmol/hr solvent, at least about 20 kmol/hr solvent, at least about 25 kmol/hr solvent, at least about 30 kmol/hr solvent, at least about 50 kmol/hr solvent, at least about 75 kmol/hr solvent, at least about 100 kmol/hr solvent, at least about 150 kmol/hr solvent, at least about 175 kmol/hr solvent, at least about 200 kmol/hr solvent, at least about 250 kmol/hr solvent, or at least about 300 kmol/hr solvent In some embodiments, the mass fraction of solvent in the recycled carbonylation catalyst stream can be at least about 0.60, at least about 0.65, at least about 070, or at least about 0.74. In some embodiments, the mole fraction of solvent in the recycled carbonylation catalyst stream can be at least about 0.60, at least about 0.65, at least about 0.70, at least about 0.75, at least about 0.80, or at least about 0.85. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can also include unreacted carbon monoxide (in about at most 0.5 kg/hr, at most about 1 kg/hr, at most about 1.2 kg/hr, at most about 1.5 kg/hr, at most 5 kg/hr, at most about 10 kg/hr, at most about 12 kg/hr, or at most about 15 kg/hr, or a mass fraction of at most about 0.001), unreacted ethylene oxide (in about at most about 10 kg/hr, at most about 20 kg/hr, at most 30 kg/hr, at most 33 kg/hr, at most about 100 kg/hr, at most about 200 kg/hr, at most 300 kg/hr, or at most 330 kg/hr or a mass fraction of between about 0.005-0.01, about 0.01-0.05, or at most about 0.014, or at most about 0.10), secondary reaction product acetaldehyde (in about at most 1 kg/hr, at most about 2 kg/hr, at most about 3.3 kg/hr, at most 10 kg/hr, at most about 20 kg/hr, or at most about 33 kg/hr or a mass fraction of at most about 0.01), secondary reaction product succinic anhydride (in about at most 1 kg/hr, at most about 2 kg/hr, at most about 3 kg/hr, at most 10 kg/hr, at most about 20 kg/hr, or at most about 30 kg/hr or a mass fraction of at most about 0.01), bPL (in about at most about 250 kg/hr, at most about 400 kg/hr, at most about 500 kg/hr, at most about 545 kg/hr, at most about 1000 kg/hr, at most

about 2500 kg/hr, at most about 4000 kg/hr, or at most about 5450 kg/hr or a mass fraction of at most about 0.1, at most about 0.15, at most about 0.2, at most about 0.22, or at most about 0.23), and carbonylation catalyst or components thereof.

[0228] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0229] In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 25 kg/hr carbonylation catalyst, at least about 35 kg/hr carbonylation catalyst, at least about 45 kg/hr carbonylation catalyst, at least about 50 kg/hr carbonylation catalyst, at least about 53 kg/hr carbonylation catalyst, at least about 100 kg/hr carbonylation catalyst, at least about 250 kg/hr carbonylation catalyst, at least about 350 kg/hr carbonylation catalyst, at least about 450 kg/hr carbonylation catalyst, at least about 500 kg/hr carbonylation catalyst, at least about 530 kg/hr carbonylation catalyst. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 0.01 kmol/hr carbonylation catalyst, at least about 0.025 kmol/hr carbonylation catalyst, at least about 0.04 kmol/hr carbonylation catalyst, at least about 0.05 kmol/hr carbonylation catalyst, at least about 0.056 kmol/hr carbonylation catalyst, at least about 0.1 kmol/hr carbonylation catalyst, at least about 0.25 kmol/hr carbonylation catalyst, at least about 0.4 kmol/hr carbonylation catalyst, at least about 0.5 kmol/hr carbonylation catalyst, or at least about 0.56 kmol/hr carbonylation catalyst. In some embodiments, the mass fraction of carbonylation catalyst in the recycled carbonylation

catalyst stream can be at least about 0.002, at least about 0.015, at least about 0.02, or at least about 0.022. In some embodiments, the mole fraction of carbonylation catalyst in the recycled carbonylation catalyst stream can be at least about 0.0002, at least about 0.0015, at least about 0.002, at least about 0.003, at least about 0.004, or at least about 0.005.

[0230] In some embodiments, the inlet to the carbonylation reaction system can receive solvent from solvent feed 1424 at least about 10000 kg/hr, at least about 11000 kg/hr, at least about 12000 kg/hr, at least about 12250 kg/hr, at least about 13000 kg/hr, at least about 25000 kg/hr, at least about 50000 kg/hr, at least about 100000 kg/hr, at least about 110000 kg/hr, at least about 120000 kg/hr, at least about 122500 kg/hr, or at least about 130000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive solvent from a solvent feed at least about 150 kmol/hr, at least about 160 kmol/hr, at least about 170 kmol/hr, at least about 180 kmol/hr, at least about 190 kmol/hr, at least about 500 kmol/hr, at least about 1000 kmol/hr, at least about 1500 kmol/hr, at least about 1600 kmol/hr, at least about 1700 kmol/hr, at least about 1800 kmol/hr, or at least about 1900 kmol/hr In some embodiments, the amount of solvent in the solvent feed to the carbonylation reaction system can be fixed to ensure the residence time in the carbonylation reaction system is at a set time. For example, the residence time can be about 1-500 minutes, about 20-450 minutes, about 30-300 minutes, about 35-200 minutes, or about 40-80 minutes. As previously discussed, in some embodiments, the solvent introduced to the carbonylation reaction system can include some recycled solvents from the carbonylation catalyst isolation system and the BPL purification system. Accordingly, in some embodiments, the inlet to the carbonylation reaction system can also receive carbon monoxide (in about 0.1-10 kg/hr, about 0.5-5 kg/hr, about 0.1-10 kg/hr, about 0.1-50 kg/hr, about 0.1-100 kg/hr, about 0.5-50 kg/hr, at most about 50 kg/hr, at most about 10 kg/hr, at most about 5 kg/hr, at most about 3 kg/hr, or at most about 1.3 kg/hr), ethylene oxide (in about 40-80 kg/hr, about 50-70 kg/hr, about 40-150 kg/hr, about 40-250 kg/hr, about 50-500 kg/hr, about 50-800 kg/hr,

at most about 800 kg/hr, at most about 500 kg/hr, about most about 250 kg/hr, 80 kg/hr, at most about 70 kg/hr, or at most about 66 kg/hr or a mass fraction of about 0.001-0.01, about 0.002-0.007, or most about 0.01, at most about 0.005), acetaldehyde (in about 1-200 kg/hr, about 1-150 kg/hr, about 1-100 kg/hr, about 1-50 kg/hr, about 1-20 kg/hr, about 5-15 kg/hr, or at most about 200 kg/hr, at most about 150 kg/hr, at most about 100 kg/hr, at most about 50 kg/hr, at most about 20 kg/hr, at most about 15 kg/hr, or at most about 11 kg/hr or a mass fraction of at most about 0.001), succinic anhydride (in about 1-100 kg/hr, about 1-50 kg/hr, 1-10 kg/hr, about 1-5 kg/hr, or at most about 50 kg/hr, at most about 10 kg/hr, 5 kg/hr, or at most about 3 kg/hr), bPL (in about at most 2000 kg/hr, at most about 1500 kg/hr, at most about 1000 kg/hr, at most about 500 kg/hr, 200 kg/hr, at most about 300 kg/hr, at most about 500 kg/hr, at most about 550 kg/hr, or at most about 600 kg/hr, or a mass fraction of at most 0.1, at most about 0.075, at most about 0.05, or at most about 0.043), and carbonylation catalyst or components thereof from the solvent feed. In some embodiments, the mass fraction of solvent from the solvent feed can be at least about 0.85, at least about 0.9, at least about 0.94, or at least about 0.95. In some embodiments, the mole fraction of solvent from the solvent feed can be at least about 0.85, at least about 0.9, at least about 0.94, or at least about 0.95.

[0231] In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a solvent feed at least about 1000 kg/hr, at least about 750 kg/hr, at least about 600 kg/hr, at least about 530 kg/hr, at least about 500 kg/hr, at least about 250 kg/hr, at least about 100 kg/hr, at least about 75 kg/hr, at least about 60 kg/hr, at least about 53 kg/hr, or at least about 50 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a solvent feed at least about 1 kmol/hr, at least about 0.8 kmol/hr, at least about 0.75 kmol/hr, at least about 0.56 kmol/hr, or at least about 0.5 kmol/hr, at least about 0.25 kmol/hr, at least about 0.1 kmol/hr, at least about 0.1 kmol/hr, at least about 0.075 kmol/hr, at least about 0.056 kmol/hr, or at least about 0.05 kmol/hr. In some

embodiments, the mass fraction of carbonylation catalyst from the solvent feed can be at least about 0.0002, at least about 0.002, at least about 0.003, or at least about 0.004.

[0232] In some embodiments, the inlet to the carbonylation reaction system can receive a solvent feed at a temperature between about 10-100°C, between about 20-50°C, between about 25-45°C, between about 30-40°C, or about 36.6°C. In some embodiments, the inlet to the carbonylation reaction system can receive a solvent feed at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Other Feed Sources

[0233] The β-propiolactone production system/production process may further include other feed sources. For example, in one variation, the β-propiolactone production system/production process further includes a Lewis base additive source.

[0234] In some embodiments, a Lewis base additive may be added to the carbonylation reactor. In certain embodiments, such Lewis base additives can stabilize or reduce deactivation of the catalysts. In some embodiments, the Lewis base additive is selected from the group consisting of phosphines, amines, guanidines, amidines, and nitrogen-containing heterocycles. In some embodiments, the Lewis base additive is a hindered amine base. In some embodiments, the Lewis base additive is a 2,6-lutidine; imidazole, 1-methylimidazole, 4-dimethylaminopyridine, trihexylamine and triphenylphosphine.

[0235] The exemplary system depicted in FIG. **14** also includes carbonylation product stream 1414, post-isolation carbonylation product stream 1416, BPL purified stream 1418, PPL product stream 1420, and GAA product stream 1422.

Reactor

[0236] In some embodiments, the carbonylation reaction system can include at least one reactor for the carbonylation reaction. In some embodiments, the carbonylation system can include multiple reactors in series and/or parallel for the carbonylation reaction. In some

embodiments, the reactor(s) can be a continuous reactor(s). Examples of suitable continuous reactors include but are not limited to tubular reactors (i.e., plug flow-type reactors), fixed bed reactors, fluid bed reactors, continuous stirred tank reactors ("CSTR"), heat exchanger reactors (e.g., shell and tube type reactor), loop reactors (e.g., Buss, jet, etc.), membrane reactors, or other reactors known to those of ordinary skill in the art. In some embodiments, the carbonylation reaction system includes one or more CSTRs. All inlets and outlets to the carbonylation reaction system can include sensors that can determine the flowrate, composition (especially water and/or oxygen content), temperature, pressure, and other variables known to those of ordinary skill in the art. In addition, the sensors can be connected to control units that can control the various streams (i.e., feed controls) in order to adjust the process based on the needs of the process determined by the sensor units. Such control units can adjust the quality as well as the process controls of the system.

[0237] In some variations, the reactor in the β-propiolactone production system/production process is configured to receive the catalyst, ethylene oxide and carbon monoxide in certain ratios. In some embodiments, the ratio of catalyst to ethylene oxide is selected, based on other reaction conditions, so that the reaction proceeds in an economical and time-feasible manner. In some embodiments, the ratio of catalyst to ethylene oxide is about 1:10000 on a molar basis. In some embodiments, the molar ratio of catalyst to ethylene oxide is about 1:5000, is about 1:2500, is about 1:2000, is about 1:1500, is about 1:1000, is about 1:750, is about 1:500, is about 1:250, is about 1:200, is about 1:150, or is about 1:100. In some embodiments, the concentration of the ethylene oxide is in the range between about 0.1 M and about 5.0 M. In some embodiments, the concentration of the ethylene oxide is in the range between about 0.5 M and about 3.0 M.

[0238] In certain embodiments, the molar ratio of carbon monoxide to ethylene oxide in the reaction stream ranges from about 0.1:1 to about 100:1. In certain embodiments, the molar

ratio of carbon monoxide to ethylene oxide in the reaction stream is about 50:1, is about 20:1, is about 10:1, is about 5:1 or is about 1:1, or within a range including any two of these ratios. In some embodiments, the ratio of carbon monoxide to ethylene oxide is selected based on other reaction conditions so that the reaction proceeds in an economical and time-feasible manner.

[0239] In some variations, the reactor in the β-propiolactone production system/production process is configured to further receive one or more additional components. In certain embodiments, the additional components comprise diluents which do not directly participate in the chemical reactions of ethylene oxide. In certain embodiments, such diluents may include one or more inert gases (e.g., nitrogen, argon, helium and the like) or volatile organic molecules such as hydrocarbons, ethers, and the like. In certain embodiments, the reaction stream may comprise hydrogen, carbon monoxide of carbon dioxide, methane, and other compounds commonly found in industrial carbon monoxide streams. In certain embodiments, such additional components may have a direct or indirect chemical function in one or more of the processes involved in the conversion of ethylene oxide to β-propiolactone and various end products. Additional reactants can also include mixtures of carbon monoxide and another gas. For example, as noted above, in certain embodiments, carbon monoxide is provided in a mixture with hydrogen (e.g., Syngas).

[0240] Because the carbonylation reaction is exothermic, the reactors used can include an external circulation loop for reaction mass cooling. In some embodiments, the reactors can also include internal heat exchangers for cooling. For example, in the case of a shell and tube type reactor, the reactors can flow through the tube part of the reactor and a cooling medium can flow through the shell of the reactor or vice versa. Heat exchanger systems can vary depending on layout, reactor selection, as well as physical location of the reactor. The reactors can employ heat exchangers outside of the reactors in order to do the cooling/heating or the

reactors can have an integrated heat exchanger such as a tube and shell reactor. For example, a CSTR can utilize a layout for heat rejection by pumping a portion of the reaction fluid through an external heat exchanger or a plug flow-type reactor can be an integrated unit that combines the reactor and the heat exchanger into a single unit. Additional reactor/heat exchanger systems and heat management systems can be found in US Patent Nos. 3,128,163; 4,759,313; 8,246,915, which are hereby incorporated by reference in their entirety. In some embodiments, heat can be removed from a CSTR by using a coolant in a reactor jacket, one or more internal cooling coils, lower temperature feeds and/or recycle streams, an external heat exchange with pump around loop, and/or other methods known by those of ordinary skill in the art. In some embodiments, heat can be removed from a plug flow type reactor or a loop reaction by using a coolant in the reactor jacket and/or internal cooling coils. Furthermore, the reaction can occur on the tube side or the shell side of a shell and tube reactor and the other side can have the cooling medium. In addition, the reactors may have multiple cooling zones with varying heat transfer areas and/or heat transfer fluid temperatures and flows.

[0241] The type of reactor employed and the type of heat exchanger employed (either external or integrated) can be a function of various chemistry considerations (e.g., reaction conversions, by-products, etc.), degree of exotherm produced, and the mixing requirements for the reaction.

[0242] Since carbonylation reactions are exothermic reactions and the BPL purification system and thermolysis requires energy, it is possible to integrate at least some of the components between the carbonylation reaction system and the BPL purification system and/or thermolysis system. For example, steam or tempered water or other appropriate heat transfer media can be produced in a heat exchanger of the carbonylation reaction system and transported to the BPL purification system for heating a distillation column for example. In addition, the BPL purification system and the carbonylation reaction system may be integrated

into a single system or unit so that the heat produced from the carbonylation reaction can be used in the BPL purification system (in an evaporator or distillation column). The steam can be generated in a heat exchanger (e.g., shell and tube heat exchanger, reactor's cooling jacket, etc) via a temperature gradient between reaction fluids and water/steam of the heat exchanger. Steam can be used for heat integration between exothermic units (carbonylation reaction, polymerization reaction) and endothermic units (BPL purification system's columns/evaporators and thermolysis reaction). In some embodiments, steam is only used for heat management and integration and will not be introduced directly into the production processes.

[0243] As previously described, water and oxygen can damage the carbonylation catalyst. As such, oxygen and water intrusion into the carbonylation system should also be minimized. As such, the reactor seals may utilize a magnetic drive, a double mechanical seal, and/or materials of construction that are compatible with the reactants and products of the carbonylation reaction but not permeable to atmosphere. In some embodiments, the materials of construction of the reactor include metals. In some embodiments, the metals can be stainless steel. In some embodiments, the metals can be carbon steel. In some embodiments, the metals can be metal alloys such as nickel alloys. In some embodiments, the metals are chosen when compatibility or process conditions dictate, e.g., high chloride content or if carbon steel catalyzes EO decomposition. In some embodiments, everything up until the polymerization reaction system can include carbon steel. One of the benefits of carbon steel over stainless steel is its cost. In some embodiments, the metals can have a surface finish so as to minimize polymer nucleation sites. The materials of construction of the reactor can also include elastomer seals. In some embodiments, the elastomer seals are compatible with the reactants and products of the carbonylation reaction but not permeable to the atmosphere. Examples of elastomer seals include but are not limited to Kalrez 6375, Chemraz 505, PTFE-encapsulated

Viton, and PEEK. The materials of construction of external parts of the carbonylation reaction system can be compatible with the environment, for example, compatible with sand, salty water, not heat absorbing, and can protect the equipment from the environment.

[0244] In some embodiments, the carbonylation reaction system is operated so as to minimize or mitigate PPL and polyethylene oxide formation prior to the polymerization reaction system. In some embodiments, the carbonylation reaction system is operated so as to avoid catalyst decomposition.

[0245] In some embodiments, the carbonylation reactor(s) can have a downstream flash tank with a reflux condenser to separate unreacted carbon monoxide as a recycled carbon monoxide stream from the carbonylation reaction system. As previously described, the recycled carbon monoxide stream can be sent to a CO compressor and/or combined with a fresh carbon monoxide feed prior to being sent back into the carbonylation reaction system. The flash tank can separate most of the CO to avoid its separation downstream, especially in the carbonylation catalyst isolation system. In some embodiments, excess gas is removed or purged from the reactor itself and thus a flash tank is not necessary.

[0246] In some embodiments, the carbonylation reactor(s) can operate at a temperature of about 40-100°C, about 50-90°C, about 60-80°C, about 65-75°C, or about 70°C. In some embodiments, the reaction temperature can range from between about -20 °C, to about 600 °C. In some embodiments, the reaction temperature is about -20 °C, about 0 °C, about 20 °C, about 40 °C, about 60 °C, about 80 °C, about 100 °C, about 200 °C, about 300 °C, about 400 °C, about 500 °C or about , about 600 °C. In some embodiments, the temperature is in a range between about 40 °C and about 120 °C. In some embodiments, the temperature is in a range between about 60 °C and about 140 °C. In some embodiments, the temperature is in a range between about 40 °C and about 80 °C. In some embodiments, the temperature is in a range between about 50 °C and about 70 °C. In some embodiments, the reactants, catalyst and solvent

are supplied to the reactor at standard temperature, and then heated in the reactor. In some embodiments, the reactants are pre-heated before entering the reactor.

[0247] In some embodiments, the carbonylation reactor(s) can operate at a pressure of about 600-1200 psig, about 700-1100 psig, about 800-1000 psig, about 850-950 psig, or about 900 psig. In some embodiments, the reaction pressure can range from between about 50 psig to about 5000 psig. In some embodiments, the reaction pressure is about 100 psig, about 200 psig, about 300 psig, about 400 psig, about 500 psig, about 600 psig, about 700 psig, about 800 psig, about 900 psig, or about 1000 psig. In some embodiments, the pressure ranges from about 50 psig to about 2000 psig. In some embodiments, the pressure ranges from about 100 psig to 1000 psig. In some embodiments, the pressure ranges from about 200 psig to about 800 psig. In some embodiments, the pressure ranges from about 800 psig to about 1600 psig. In some embodiments, the pressure ranges from about 1500 psig to about 3500 psig. In some embodiments, the pressure ranges from about 3000 psig to about 5500 psig. In some embodiments, the reaction pressure is supplied entirely by the carbon monoxide. For example, carbon monoxide is added to the reactor at high pressure to increase pressure to the reaction pressure. In some embodiments, all reactants, solvent and catalyst are supplied to the reactor at reaction pressure.

[0248] In some embodiments, the reaction is maintained for a period of time sufficient to allow complete, near complete reaction of the ethylene oxide to carbonylation products or as complete as possible based on the reaction kinetics and or reaction conditions. In some embodiments, the reaction time is a residence time in the carbonylation reactor in step (a). In certain embodiments, the residence time is about 12 hours, about 8 hours, about 6 hours, about 3 hours, about 2 hours or about 1 hour. In certain embodiments, the residence time is about 30 minutes, about 20 minutes, about 15 minutes, about 10 minutes, about 5 minutes, about 3

minutes, about 2 minutes, or about 1 minute. In certain embodiments, the residence time is less than 1 minute.

[0249] The chemistry involved in a carbonylation reaction system can include, but are not limited to, the following three reactions: (1) CO + EO → bPL; (2) EO → acetaldehyde; (3) bPL → succinic anhydride. The conversions for the three reactions may vary depending on many factors including amount of reactants, amount of catalyst, temperature, pressure, flow rate, etc. However, the first reaction can have an EO conversion of about 0.2-0.999, about 0.5-0.95, about 0.6-0.9, about 0.7-0.8, or about 0.75. The second reaction can have an EO conversion of about 0-0.1, about 0.001-0.02, about 0.002-0.01, or about 0.005. The third reaction can have a bPL conversion of about 0.0002-0.02, about 0.0005-0.01, about 0.001-0.003, or about 0.002.

[0250] FIG. **15** illustrates an exemplary embodiment of a carbonylation reaction system disclosed herein. Carbonylation reaction system **1513** can include carbonylation reaction system inlet **1509** for carbonylation reactor **1525**. As previously described, the inlet can be made up of multiple inlets or feeds into the reaction system. In addition, carbonylation reaction system **1513** includes flash tank **1526** with condenser **1527**. Flash tank **1526** and condenser **1527** separate the reactor product stream into recycled carbon monoxide stream **1510** and carbonylation product stream **1514**.

Carbonylation Product Stream (i.e., BPL Product Stream)

[0251] In some embodiments, the carbonylation product stream includes at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 8000 kg/hr bPL, at least about 12000 kg/hr bPL, at least about 16000 kg/hr bPL, at least about 20000 kg/hr bPL, at least about 25000 kg/hr bPL, at least about 30000 kg/hr bPL, at least about 35000 kg/hr bPL, at least about 36380 kg/hr bPL, or at least about 40000 kg/hr bPL. In some

embodiments, the carbonylation product stream includes between about 2000 kg/hr bPL and about 4000 kg/hr bPL, about 2500 kg/hr bPL and about 4000 kg/hr bPL, about 3000 kg/hr bPL and about 4000 kg/hr bPL, about 3500 kg/hr bPL and about 4000 kg/hr bPL, about 3638 kg/hr bPL and about 4000 kg/hr bPL, between about 2000 kg/hr bPL and about 40000 kg/hr bPL, about 2500 kg/hr bPL and about 40000 kg/hr bPL, about 3000 kg/hr bPL and about 40000 kg/hr bPL, about 3500 kg/hr bPL and about 40000 kg/hr bPL, about 3638 kg/hr bPL and about 40000 kg/hr bPL, about 4000 kg/hr bPL and about 40000 kg/hr bPL, about 8000 kg/hr bPL and about 40000 kg/hr bPL, about 12000 kg/hr bPL and about 40000 kg/hr bPL, about 16000 kg/hr bPL and about 40000 kg/hr bPL, about 20000 kg/hr bPL and about 40000 kg/hr bPL, about 25000 kg/hr bPL and about 40000 kg/hr bPL, about 30000 kg/hr bPL and about 40000 kg/hr bPL, or about 35000 kg/hr bPL and about 40000 kg/hr bPL.

[0252] In some embodiments, the carbonylation product stream includes at least about 30 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 45 kmol/hr bPL, at least about 50 kmol/hr bPL, at least about 55 kmol/hr bPL, at least about 100 kmol/hr bPL, at least about 200 kmol/hr bPL, at least about 300 kmol/hr bPL, at least about 400 kmol/hr bPL, at least about 450 kmol/hr bPL, at least about 500 kmol/hr bPL, or at least about 550 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the carbonylation product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.2-0.23, at least about 0.15, at least about 0.2, or at least about 0.224. In some embodiments, the mole fraction of bPL in the carbonylation product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.21-0.23, at least about 0.15, at least about 0.2, or at least about 0.22. The carbonylation product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005-0.05, about 0.02-0.045, about 0.04, at most about 0.014, at most about 0.02, or at most about 0.05), unreacted carbon monoxide (in mass fraction of about 0.0005-0.01, at most about 0.01, or at most about 0.02), acetaldehyde (in mass fraction of about 0.0005-0.001, at most about

0.001, or at most about 0.002), succinic anhydride (in mass fraction of about 0.0005-0.001, at most about 0.001, or at most about 0.002), carbonylation catalyst (in about 40-640 kg/hr, about 45-600 kg/hr, about 50-600 kg/hr, about 50-300 kg/hr, about 50-100 kg/hr, about 40-64 kg/hr, about 45-60 kg/hr, about 50-60 kg/hr, at most 54.8 kg/hr, at most about 60 kg/hr, at most 300 kg/hr, or at most 600 kg/hr or a mass fraction of about 0.001-0.005, about 0.002-0.004, at most about 0.003, or at most about 0.004), and the remainder solvent. In some embodiments, the carbonylation product stream can include sufficient ethylene oxide so as to prevent anhydride formation.

[0253] In some embodiments, the carbonylation product stream from the carbonylation reaction system can have a temperature of about 50-100°C, about 60-90°C, about 65-75°C, or about 70°C. In some embodiments, the carbonylation product stream can have a pressure of about 1-5 bar, about 2-4 bar, or about 3 bar.

[0254] In some embodiments, the carbonylation reaction system has a selectivity of at least about 95%, at least about 97%, at least about 99%, at least about 99.5%, or at least about 99.8%. In some embodiments, the carbonylation reaction system has a yield of at least about 90%, at least about 95%, at least about 98%, at least about 99%, or at least about 99.5%. In some embodiments, the selectivity of bPL is the ratio of bPL yield to ethylene oxide conversion, wherein the bPL yield is measured relative to ethylene oxide. In other embodiments, the selectivity of bPL is the ratio of bPL yield to carbon monoxide conversion, wherein the bPL yield is measured relative to carbon monoxide.

Carbonylation Catalyst Recycle System

[0255] With reference again to FIG. **1**, the carbonylation catalyst recycle system may be employed to recover at least a portion of the carbonylation catalyst, or components thereof, present in the β-propiolactone product stream. Such recovered carbonylation catalyst may be recycled and reused in the β-propiolactone production system/production process.

[0256] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0257] Any suitable methods and techniques known in the art may be used to recover at least a portion of the carbonylation catalyst present in the β-propiolactone product stream. Such methods and techniques may include, for example, nanofiltration (as depicted in FIG. **1**), distillation, liquid-liquid extraction, ionic liquids, and ion exchange, or adsorption. Combinations of methods and techniques described herein may also be employed.

Nanofiltration

[0258] In some embodiments, the carbonylation catalyst recycle system involves the use of nanofiltration. For example, a nanofiltration membrane may be used. In some variations, the nanofiltration membrane is an organic solvent-stable nanofiltration membrane. Although any nanofiltration membrane may be used in combination with any organic solvent or organic solvent system compatible with the carbonylation reaction, the nanofiltration membrane may be selected in combination with the organic solvent or solvents such that the process achieves predetermined levels of lactone formation and catalyst-lactone separation. In some variations, the nanofiltration membrane is a polymeric nanofiltration membrane, while in other variations, the nanofiltration membrane is a ceramic nanofiltration membrane.

[0259] In some embodiments, the nanofiltration membrane is a polymeric membrane. Any suitable polymeric membranes may be used in the methods described herein. For example, in some variations, the polymeric membrane comprises polyimides, polyamide-imides, silicone-

coated polyamide composites, polyacrylonitriles, polydimethylsiloxane films on polyacrylonitrile supports, silcones, polyphosphazenes, polyphenylene sulfide, polyetheretherketone, or polybenzimidazol. In certain variations, the polymeric membrane has a silicone backbone.

[0260] In certain variations, the polymeric membrane is selected from polyimides, including those marketed under the trademark STARMEM by Membrane Extraction Technology Ltd (Wembley, UK) and integrally skinned asymmetric membranes made from polyimides, polyamide-imides, silicone-coated polyamide composites, polyacrylonitriles, polydimethylsiloxane films on polyacrylonitrile supports, silcones, polyphosphazenes, polyphenylene sulfide, polyetheretherketone, and polybenzimidazol. In some embodiments, the organic solvent is tetrahydrofuran and the nanofiltration membrane is an integrally skinned asymmetric polyimide membrane made from Lenzing P84 or a ST ARMEM® polyimide membrane. In some embodiments, the organic solvent is diethyl ether and the nanomembrane is a silicone-coated polyamide composite. In some embodiments, the nanofiltration membrane is a commercially available membrane. In other embodiments, the nanofiltration membrane is an integrally skinned asymmetric polyimide membrane made from Lenzing P84 and manufactured by GMT Membrantechnik GmbH (Rheinfelden, Germany). In some other embodiments, the nanofiltration membrane is a STARMEM® polyimide membrane from Membrane Extraction Technology Ltd (Wembley, UK) and the nanofiltration step is performed at a temperature under 50 °C and a pressure under 60 bar. In still other embodiments, the nanofiltration membrane is a silicone-coated organic solvent resistant polyamide composite nanofiltration membrane as disclosed in U.S. Patent No. 6,887,380, incorporated herein by reference.

[0261] In other variations, the nanofiltration membrane is a ceramic membrane comprising inorganic materials.

[0262] Nanofiltration membranes of various configurations may be employed in the carbonylation catalyst recycling system. For example, in some embodiments, the membrane is a plate-and-frame membrane. With reference to FIG. **3**, exemplary carbonylation catalyst recycle system **300** that uses membrane **310** is depicted. Feed **302** may include, for example, β-propiolactone, carbonylation solvent, small amounts of ethylene oxide and carbon monoxide, carbonylation catalyst, and by-products (such as acetaldehyde and succinic anhydride). Feed **302** is transferred to membrane via pumps **306** and **308**. Sensor **304** is positioned before pump **306** to regulate the rate at which feed **302** is pumped through membrane **310**. In some variations, sensor **304** may be a ultra-violet (UV) sensor. Other suitable sensors may also be employed. Feed **302** passes through membrane **310** by way of the transmembrane pressure, varied according to the pump set points. In some variations, membrane **310** is a plate-and-frame membrane, as depicted in FIG. **3**. However, in other variations, other suitable membranes may be used. For example, in other variation, membrane **310** of carbonylation catalyst recycle system **300** may be a spiral wound membrane or a tubular membrane, and such alternative configurations are discussed in further detail below.

[0263] With reference again to FIG. **3**, membrane **310** produces permeate stream **316** and retentate stream **324**. Permeate stream **316** may include, for example, β-propiolactone, carbonylation solvent, small amounts of ethylene oxide and carbon monoxide, by-products (such as acetaldehyde and succinic anhydride), and trace amounts of carbonylation catalyst. Further, permeate stream **316** may have a permeability of at least 0.5 L/m^2 hr bar, at least 0.6 L/m^2 hr bar, at least 0.7 L/m^2 hr bar, at least 0.8 L/m^2 hr bar, at least 0.9 L/m^2 hr bar, at least 1.0 L/m^2 hr bar, at least 1.1 L/m^2 hr bar, at least 1.2 L/m^2 hr bar, at least 1.3 L/m^2 hr bar, at least 1.4 L/m^2 hr bar, at least 1.5 L/m^2 hr bar, at least 1.6 L/m^2 hr bar, at least 1.7 L/m^2 hr bar, at least 1.8 L/m^2 hr bar, at least 1.9 L/m^2 hr bar, at least 2 L/m^2 hr bar, at least 2.5 L/m^2 hr bar, at least 3 L/m^2 hr bar, at least 3.5 L/m^2 hr bar, or at least 4 L/m^2 hr bar; or between 0.5 L/m^2 hr bar and 5

L/m^2 hr bar, or between 3 L/m^2 hr bar and 4.5 L/m^2 hr bar; or between 0.5 L/m^2 hr bar and 10 L/m^2 hr bar, or between 3 L/m^2 hr bar and 10 L/m^2 hr bar. In some variations, permeability (or membrane permeability) refers to volumetric flow rate of material that permeates through a specified surface area at a specified transmembrane pressure (TMP). In some variations, the transmembrane pressure is the pressure difference between the retentate side of the membrane and the permeate side of the membrane. In some embodiments, the relationship can be expressed as Permeability = Volumetric flow rate / (Surface Area x TMP). In some embodiments, permeability may be determined by measuring the flow rate of material which permeates across a membrane sample of known surface area at a known TMP.

[0264] Sensor **312** is positioned after membrane **310** to analyze the contents of permeate stream **316**. In some variations, sensor **312** may be a UV sensor. Other suitable sensors may also be employed.

[0265] Carbonylation catalyst recycle system **300** is configured to achieve a catalyst rejection of at least 80%, at least 85%, at least 90%, at least 91%, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%, at least 99.1%, at least 99.2%, at least 99.3%, at least 99.4%, at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%, or 100%. In some variations, catalyst rejection refers to the percentage (by mass) of catalyst which permeates through the membrane compared to that which does not and is retained on the retentate side of the membrane. Catalyst rejection may be determined by any suitable method in the art, including, for example, using analytical instruments to detect catalyst concentrations at the membrane feed, permeate and retentate.

[0266] With reference again to FIG. **3**, pressure control valve **314** is positioned after sensor **312** and biased to upstream flash units. In some embodiments, pressure control valve (PCV) 314 can be used to control transmembrane pressure (TMP) which may affect performance of the membrane. Sensor 312 may detect catalyst rejection and provide a feedback signal to PCV

314 to make adjustments for system performance. PCV 314 may in some embodiments detect the pressure of the upstream flash tank and prevent volatile species (for example, carbon monoxide) from vaporizing as pressure changes across the membrane. Vaporization or flashing across the membrane may affect the durability of the membrane.

[0267] Retentate stream **324** may include, for example, carbonylation solvent, β-propiolactone, and carbonylation catalyst. Pump **322** may be used to transfer retentate stream **324** to the β-propiolactone production system/production process described herein (*e.g.*, to a carbonylation reactor of the β-propiolactone production system/production process). In some embodiments, catalyst may deactivate as it is circulated through the membrane system on the retentate side (for example, with exposure to oxygen or water). In certain embodiments, a portion of the retentate stream is purged for a period of time to avoid accumulation of deactivated catalyst within the system. Valve **320** is configured to purge the system and bleed **326**.

[0268] As discussed above, while FIG. **3** depicts the use of a plate-and-frame membrane, other membrane configurations may be employed. For example, in other embodiments, the membrane is a spiral wound membrane. In yet other embodiments, the membrane is a tubular membrane. In still other embodiments, the membrane is a pleated sheet membrane.

[0269] In one variation, the membrane is a polymeric membrane in a plate and frame configuration. In another variation, the membrane is a polymeric membrane in a spiral wound configuration. In yet another variation, the membrane is a ceramic membrane in a tubular configuration.

[0270] While FIG. **3** depicts the use of one membrane, in other variations, a plurality of membranes may be used. For example, at least two membranes connected in series may be used. In one variation, a plurality of plate-and-frame membranes connected in series may be used. In other variations, a plurality of spiral wound membranes connected in series may be

used. In other variations, a plate-and-frame membrane may be connected in series with a spiral wound membrane. It should be understood that the membrane configurations may be in series, in parallel, or in a combination of series and parallel. For example, in some embodiments, the membranes are configured in a "Christmas tree" configuration.

[0271] In one embodiment, the nanofiltration membrane is a polymeric, spiral wound membrane with a silicone backbone, carbonylation catalyst rejection rate of at least 99%, and permeability of at least 1 L/m^2 hr bar.

Distillation

[0272] In other embodiments, the carbonylation catalyst recycle system involves a distillation apparatus.

[0273] In some variations, the distillation apparatus recover at least a portion of the carbonylation catalyst present in the β-propiolactone product stream using a multi-solvent system. For example, in one variation, a two-solvent system may be used, wherein the first solvent has a boiling point above 166°C and may serve as the carrier of the catalyst, and the second solvent is selected to facilitate the carbonylation reaction.

[0274] In other variations, the distillation may include heating the β-propiolactone product stream to volatilize at least a portion of the β-propiolactone and/or the solvent to form a distillate, removing the distillate, and condensing the distillate. In other embodiments, the distillation is a vacuum distillation, wherein the distillate is formed by reducing the pressure of the β-propiolactone product stream. In certain embodiments, vacuum distillation allows at least a portion of the carbonylation catalyst to be removed from the β-propiolactone product stream without degradation of the catalyst at higher temperatures. In other variations, the distillation is performed by both increasing the temperature and decreasing the pressure of the β-propiolactone product stream. The carbonylation catalyst remaining the in the retained mixture after distillation can then be isolated for reuse in the carbonylation reaction using any methods

known in the art, including, for example, solvent-solvent extraction, nanofiltration, ionic liquids, or adsorption.

Liquid-Liquid Extraction

[0275] In other embodiments, the carbonylation catalyst recycle system involves a liquid-liquid extraction apparatus.

[0276] In some variations, the liquid-liquid extraction apparatus employs an extraction solvent in which the catalyst (or a component of the catalyst) is soluble or at least partially soluble. In other variations, the extraction solvent is one in which the β-propiolactone is soluble or at least partially soluble, but which has little tendency to dissolve the carbonylation catalyst (or one or more components of the carbonylation catalyst). In either case, the use of the extraction solvent results in the formation of two phases. In certain embodiments, the extraction solvent is a highly polar solvent such as water or an ionic liquid. In certain embodiments, the extraction solvent is supercritical CO_2. In certain embodiments, the extraction solvent is water or an aqueous solution. In certain embodiments, the extraction solvent is an ionic liquid. In certain embodiments where the solvent is an ionic liquid, the ionic liquid has a formula $[Cat^+][X^-]$ wherein $[Cat^+]$ refers to one or more organic cationic species; and [X"] refers to one or more anions. In certain embodiments, $[Cat^+]$ is selected from the group consisting of: ammonium, tetralkylammonium, benzimidazolium, benzofuranium, benzothiophenium, benzotriazolium, borolium, cinnolinium, diazabicyclodecenium, diazabicyclononenium, 1 ,4-diazabicyclo[2.2.2]octanium, diazabicyclo-undecenium, dithiazolium, furanium, guanidinium, imidazolium, indazolium, indolinium, indolium, morpholinium, oxaborolium, oxaphospholium, oxazinium, oxazolium, iso-oxazolium, oxothiazolium, phospholium, phosphonium, phthalazinium, piperazinium, piperidinium, pyranium, pyrazinium, pyrazolium, pyridazinium, pyridinium, pyrimidinium, pyrrolidinium, pyrrolium, quinazolinium, quinolinium, iso-quinolinium, quinoxalinium, quinuclidinium,

selenazolium, sulfonium, tetrazolium, thiadiazolium, iso-thiadiazolium, thiazinium, thiazolium, iso-thiazolium, thiophenium, thiuronium, triazinium, triazolium, iso-triazolium, uronium, and any combination of two or more of these. In accordance with the present invention, [X^-] may comprise an anion selected from halides, sulphates, sulfonates, sulfonimides, phosphates, phosphonates, carboxylates, CN^-, NO_3^-, NO_2^-, BF_4^- and PF_6^-.

[0277] In some embodiments, the extraction solvent includes pentane, cyclohexane, hexane, heptane, tetrahydrofuran, p-dioxane, 4-methyl-1,3-dioxolan-2-one, N,N-dimethylformamide, 1-methyl-2-pyrrolidinone, or sulfolane, or any combinations thereof. In one embodiment, the extraction solvent includes sulfolane and hexane. In another embodiment, the liquid-liquid extraction solvent includes sulfolane, hexane, and dioxane.

Precipitation

[0278] In certain embodiments, the carbonylation catalyst recycle system is configured to precipitate the carbonylation catalyst. Precipitation of the carbonylation catalyst may be accomplished by any known methods and techniques. Suitable means of precipitating the catalyst will be apparent to the skilled chemist and may include, but are not limited to: adding a solvent to the β-propiolactone product stream in which the catalyst (or a component thereof) is poorly soluble, cooling the β-propiolactone product stream, adding a material that interacts with the catalyst (or a component thereof) to form an insoluble adduct, removing solvent, excess feedstock, or carbon monoxide from the β-propiolactone product stream, and combinations of any two or more of these. In certain embodiments where the step of treating the β-propiolactone product stream to separate a portion of the carbonylation catalyst entails precipitation, the precipitation step comprises adding a solvent in which the catalyst (or a component of the catalyst) is poorly soluble. In certain embodiments, a non-polar solvent such as an aliphatic hydrocarbon, an aromatic hydrocarbon, or condensed phase CO_2 is added to precipitate the catalyst. In certain embodiments, a solvent selected from butane, pentane,

hexane, heptane, octane, cyclopentane, cyclohexane, decalin, higher alkanes, and mixtures of two or more alkanes is added to the β-propiolactone product stream to precipitate the catalyst or a catalyst component. In certain embodiments, a solvent selected from benzene, toluene, xylene, mesitylene, chlorobenzene, or other substituted benzene compounds is added to the β-propiolactone product stream to precipitate the catalyst or a catalyst component. In certain embodiments, supercritical CO_2 is added to the β-propiolactone product stream to precipitate the catalyst or a catalyst component. In certain embodiments where the carbonylation catalyst comprises the combination of a Lewis acidic metal complex and a metal carbonyl compound and a non-polar solvent is added to the β-propiolactone product stream, this causes precipitation of the Lewis acidic metal complex but leaves at least a portion of the metal carbonyl component of the catalyst behind in the β-propiolactone product stream. In embodiments where the catalyst is precipitated, the step of separating the carbonylation catalyst typically includes further steps to remove the precipitate from the product stream, such isolation steps are well known in the art and can include, but are not limited to filtration, sedimentation, centrifugation, coagulation, and combinations of two or more of these.

Adsorption

[0279] In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by adsorbing the carbonylation catalyst or components thereof. In some variations, adsorption can entail treating the product streams containing carbonylation catalyst with a solid adsorbing material. Suitable solid adsorbing materials may include inorganic substances, activated carbon, polymers, resins, or any combination of two or more of these. Suitable inorganic adsorbing materials may include silica gel, silicate minerals, clays, diatomaceous earth, Fuller's earth, ceramics, zirconias, molecular sieves and the like. Suitable polymers may include polystyrenes, polyacrylonitrile, polyimides, polyolefins, polyesters, polyethers, polycarbonates, polyisocyanates, and the like. Such polymers may

optionally include additional chemical functional groups to enhance their ability to adsorb carbonylation catalysts or catalyst components. Such functional groups may include acids (*e.g.*, sulfonic or carboxylic acids), coordinating groups (*e.g.*, amine, thiol, phosphine, nitrile, or boron groups), and/or bases, (*e.g.*, amine groups or nitrogen heterocycles). In certain cases, the adsorbing materials (*e.g.*, whether inorganic or polymeric) are acidic, basic, or have undergone chemical treatments to enhance the affinity of the catalyst. In embodiments where carbonylation catalyst is removed from the product streams containing carbonylation catalyst by adsorption, the adsorbent can be contacted with the product stream by any conventional method. This includes, but is not limited to: flowing the product streams containing carbonylation catalyst through a fixed bed of adsorbent; flowing the product streams containing carbonylation catalyst through a fluidized bed of adsorbent; flowing the product streams containing carbonylation catalyst through fabrics, meshes, or filtration plates comprising the adsorbent material; or slurrying the product streams containing carbonylation catalyst with the adsorbent material (typically followed by filtration, centrifugation, sedimentation or the like to remove the adsorbent from the product stream).

[0280] In embodiments where the β-propiolactone product stream is flowed through a column of adsorbent, it may be desirable to provide a plurality of such columns in parallel with a provision to switch the flow from one column to another. Thus when one column of adsorbent becomes saturated with catalyst, it can be switched out of the flow path and the flow diverted to a fresh column—in certain embodiments, the interval of time from when a column is placed in the flow path to when it is switched out of the flow path corresponds to the "first time interval" recited in the methods described herein. Where an adsorbent is used to remove catalyst from the β-propiolactone product stream, the inventive methods will typically include a step of desorbing the catalyst or catalyst component(s) from the adsorbent. Such desorption methods are well known in the art and will vary depending on the identity of the adsorbant and

the catalyst. Desorption can include treating with a polar solvent or solute which displaces the catalyst or catalyst component, or can comprise a reactive process where a reagent is added to the adsorbed catalyst to regenerate it or form a species which is less adhered to the adsorbing solid.

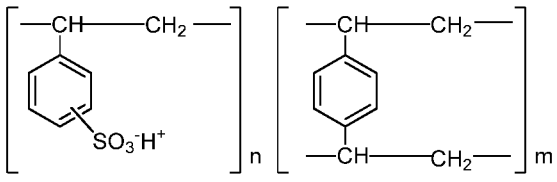
Ion Exchange

[0281] In certain embodiments, the carbonylation catalyst recycle system may be configured to separate the carbonylation catalyst by ion exchange of the carbonylation catalyst or components thereof. In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by treating the β-propiolactone product stream with ion exchange materials. The ion exchange materials may be, for example, cationic, anionic, amphoteric, Lewis basic, Lewis acidic, or may comprise chelating groups. In certain embodiments, the ion exchange material may be a cation exchanger. In certain embodiments, functional groups on the cation exchange materials may be selected from: $-SO_3$, PO_3^{2-}, –COOH, $-C_6H_4OH$, –SH, $-AsO_3$, or $-SeO_3$, or combinations of two or more of these. In certain embodiments, functional groups on the cation exchange materials comprise $-SO_3$

[0282] In certain embodiments, the ion exchange material may be an anion exchanger. In certain embodiments, functional groups on the anion exchange materials may be selected from: $-N^+(alkyl)_3$, $-N^+(CH_3)_3$, $-N^+(CH_3)_2C_2H_4OH$, $-N^+(CH_3)_2C_2H_5$, $-P^+(alkyl)_3$, $-P^+(aryl)_3$,–$P^+(C_4H_9)_3$, or $-P^+(Ph)_3$, or combinations of two or more of these. In certain embodiments, functional groups on the anion exchange materials comprise $-N^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(aryl)_3$.

[0283] In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by anion exchange and cation exchange. In certain embodiments, where the carbonylation catalyst comprises the combination of a cationic Lewis

acid and an anionic metal carbonyl, each is removed separately and the method comprises treating the β-propiolactone product stream with a cation exchange material to remove the Lewis acid and an anion exchange material to remove the metal carbonyl. In certain embodiments the anion and cation exchange are performed concomitantly. In certain embodiments, the anion and cation exchange are performed sequentially. In certain embodiments, the anion exchange is performed first followed by cation exchange. In certain embodiments, the cation exchange is performed first followed by anion exchange. In certain embodiments, an ion exchange material used in the separation step comprising an organic ion exchange resin may prove useful. Organic ion exchange resins generally possess a three dimensional structure, the matrix. Functional groups maybe attached to the structure, or directly incorporated in the polymeric chains. The matrix may be constructed from linear polymeric chains cross-linked with each other by relatively short links. By way of example, in various aspects, the present disclosure includes the use of ion exchange materials comprised of sulphonated polystyrene cross-linked with divinylbenzene:



[0284] In various aspects, ion exchange materials may take the form of gels, or gel resins, distributed across a bead, or other support substrate. In various aspects, ion exchange materials may take the form of macroporous resins which have a heterogeneous structure consisting of two phases, a gel region comprised of polymers and macroscopic permanent pores. In various embodiments of the present disclosure, the ion exchange materials comprise macroreticular resins which are additionally macroporous resins in which the gel regions consist of a plurality of bead micro-grains. Ion exchange materials may comprise a wide variety of morphologies and forms, including variations in porosity and other surface properties. In various aspects,

materials can be formed into, but not limited to beads, pellets, spheres, spheroids, rings, hollow cylinders, blocks, fibers, meshes, membranes, textiles.

[0285] In various aspects, the bead size may be widely distributed, or may be very narrow, so-called mono-disperse resins. In embodiments where catalyst is removed from the β-propiolactone product stream by ion exchange, the ion exchange material can be contacted with the product stream by any conventional method. This includes, but is not limited to: flowing the β-propiolactone product stream through a fixed bed of a solid ion exchange material (i.e. in the form of beads, granules or other particles); flowing the β-propiolactone product stream through a fluidized bed of adsorbent, flowing the β-propiolactone product stream through fabrics, meshes, or filtration plates comprising the ion exchange material, or slurrying the β-propiolactone product stream with the ion exchange material (typically followed by filtration, centrifugation, sedimentation or the like to remove the ion exchange material from the product stream). In embodiments where the β-propiolactone product stream is flowed through a packed column of ion exchange material, it may be desirable to provide a plurality of such columns in parallel with a provision to switch the flow from one to another periodically. Thus when one column of ion exchange material becomes saturated with catalyst, it can be switched out of the flow path and the flow diverted to a fresh column. In certain embodiments, the interval of time from when a column is placed in the flow path to when it is switched out of the flow path corresponds to the "first time interval" recited in the methods described herein.

[0286] Where an ion exchange material is used to remove catalyst from the β-propiolactone product stream, the inventive methods will typically include a subsequent step of removing the catalyst or catalyst component(s) from the ion exchange material. Such removal methods are well known in the art and typically involve contacting the ion exchange resin with a strong solution of a salt, the anion or cation of which will displace the catalyst component from the

ion exchange material. The specifics of this removal step may vary depending on the identity of the adsorbent and the catalyst, but suitable methods are known to those skilled in the art.

Ionic Liquids

[0287] In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by using ionic liquids. For example, in some embodiments, In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst using an ionic liquid to form a biphasic system comprising an ionic liquid phase and a β-propiolactone product stream. At least a portion of the catalyst (or a component thereof) is extracted into the ionic liquid phase, such that the concentration of catalyst is reduced in the reaction product phase. The ionic liquid phase comprising at least a portion of the carbonylation catalyst is then removed, the carbonylation catalyst is isolated from the ionic liquid phase using any suitable methods known in the art, and the isolated carbonylation catalyst is recycled back into the carbonylation reactor. For example, in some embodiments the carbonylation catalyst is isolated from the ionic liquid phase using, nanofiltration or precipitation. It may also be possible at times to use an ion exchange resin for such separation.

[0288] Any suitable ionic liquid known in the art may be used. In some embodiments, a mixture of ionic liquids is used.

Materials of Construction

[0289] The materials of construction suitable for the carbonylation catalyst recycling system may use any materials that are compatible with, for example, the membrane used. In some variations, the carbonylation catalyst recycling system has inert, metal surfaces, for example, to reduce or eliminate polymer nucleation sites.

[0290] In other variations, the carbonylation catalyst recycling system may use elastomer seals that are compatible with ethylene oxide, carbon monoxide and/or β-propiolactone, and

has little to no permeability to atmosphere. Examples may include: Kalrez 6375, Chemraz 505, PTFE encapsulated Viton, and PEEK.

[0291] In yet other variations, the materials of construction of external parts of the carbonylation catalyst recycling system may be compatible with the environment, including, for example, sand and salty water, and is not heat absorbing. Further, safety interlocks and safe operating parameters may be employed. For example, the carbonylation catalyst recycling system may be configured to mitigate polypropiolactone formation prior to the polypropiolactone production system/production process, and/or to avoid catalyst decomposition (*e.g.*, by addition of CO pressure on permeate or retentate side).

β-Propiolactone Product Stream Entering Carbonylation Catalyst Recycling System

[0292] With reference again to FIG. **1**, the β-propiolactone product stream from the β-propiolactone production system/production process is transferred to the carbonylation catalyst recycling system. In some embodiments, the β-propiolactone product stream includes at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 5000 kg/hr bPL, at least about 1000 kg/hr bPL, at least about 20000 kg/hr bPL, at least about 35000 kg/hr bPL, at least about 36380 kg/hr bPL, or at least about 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes about 2000 kg/hr bPL, about 2500 kg/hr bPL, about 3000 kg/hr bPL, about 3500 kg/hr bPL, about 3638 kg/hr bPL, about 4000 kg/hr bPL, about 5000 kg/hr bPL, about 1000 kg/hr bPL, about 20000 kg/hr bPL, about 35000 kg/hr bPL, about 36380 kg/hr bPL, or about 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes between about 2000 kg/hr bPL and 4000 kg/hr bPL, between about 2500 kg/hr bPL and 4000 kg/hr bPL, between about 3000 kg/hr bPL and 4000 kg/hr bPL, between about 3500 kg/hr bPL and 4000 kg/hr bPL, between about 3638 kg/hr bPL and 4000 kg/hr bPL, between about 2000 kg/hr bPL and 40000 kg/hr bPL, between about

2500 kg/hr bPL and 40000 kg/hr bPL, between about 3000 kg/hr bPL and 40000 kg/hr bPL, between about 3500 kg/hr bPL and 40000 kg/hr bPL, between about 3638 kg/hr bPL and 40000 kg/hr bPL, between about 4000 kg/hr bPL and 40000 kg/hr bPL, between about 5000 kg/hr bPL and 40000 kg/hr bPL, between about 1000 kg/hr bPL and 40000 kg/hr bPL, between about 20000 kg/hr bPL and 40000 kg/hr bPL, between about 35000 kg/hr bPL and 40000 kg/hr bPL, between about 36380 kg/hr bPL and 40000 kg/hr bPL, or between about 40000 kg/hr bPL and 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes at least about 30 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 45 kmol/hr bPL, at least about 50 kmol/hr bPL, at least about 55 kmol/hr bPL, at least about 100 kmol/hr bPL, at least about 200 kmol/hr bPL, at least about 300 kmol/hr bPL, at least about 400 kmol/hr bPL, at least about 450 kmol/hr bPL, at least about 500 kmol/hr bPL, or at least about 550 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.2-0.23, at least about 0.15, at least about 0.2, or at least about 0.224. In some embodiments, the mole fraction of bPL in the β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.21-0.23, at least about 0.15, at least about 0.2, or at least about 0.22. The β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005-0.05, about 0.01-0.045, about 0.04, at most about 0.014, at most about 0.02, or at most about 0.05), unreacted carbon monoxide (in mass fraction of about 0.0005-0.01, at most about 0.01, or at most about 0.02), acetaldehyde (in mass fraction of about 0.0005-0.005, at most about 0.005, or at most about 0.01), succinic anhydride (in mass fraction of about 0.0005-0.005, at most about 0.005, or at most about 0.001), carbonylation catalyst (in about 40-640 kg/hr, 300-640 kg/hr, 40-300 kg/hr, 40-64 kg/hr, about 45-60 kg/hr, about 50-60 kg/hr, at most 54.8 kg/hr, at most 60 kg/hr, at most 100 kg/hr, at most 300 kg/hr, or at most about 600 kg/hr or a mass fraction of about 0.001-0.005, about 0.002-0.004, at most about 0.003, or at most

about 0.004), and the remainder solvent. In some embodiments, the β-propiolactone product stream includes carbonylation catalyst components (in about 40-640 kg/hr, 300-640 kg/hr, 40-300 kg/hr, 40-64 kg/hr, about 45-60 kg/hr, about 50-60 kg/hr, at most 54.8 kg/hr, at most 60 kg/hr, at most 100 kg/hr, at most 300 kg/hr, or at most about 600 kg/hr or a mass fraction of about 0.001-0.005, about 0.002-0.004, at most about 0.003, or at most about 0.004).

[0293] In some embodiments, the β-propiolactone product stream from the β-propiolactone production system/production process can have a temperature of about 40-100°C, about 50-90°C, about 65-75°C, or about 70°C. In some embodiments, the β-propiolactone product stream can have a pressure of about 1-15 bar, about 2-10 bar, or about 7 bar.

β-Propiolactone Product Stream Exiting Carbonylation Catalyst Recycling System

[0294] In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system includes at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3100 kg/hr bPL, at least about 3200 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 5000 kg/hr bPL, at least about 1000 kg/hr bPL, at least about 20000 kg/hr bPL, or at least about 35000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes about 2000 kg/hr bPL, about 2500 kg/hr bPL, about 3000 kg/hr bPL, about 3500 kg/hr bPL, about 3638 kg/hr bPL, about 4000 kg/hr bPL, about 5000 kg/hr bPL, about 1000 kg/hr bPL, about 20000 kg/hr bPL, about 35000 kg/hr bPL, about 36380 kg/hr bPL, or about 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system includes between about 2000 kg/hr bPL and 3500 kg/hr bPL, between about 2500 kg/hr bPL and 3500 kg/hr bPL, between about 3000 kg/hr bPL and 3500 kg/hr bPL, between about 2000 kg/hr bPL and 35000 kg/hr bPL, between about 2500 kg/hr bPL and 35000 kg/hr bPL, between about 3000 kg/hr bPL and 35000 kg/hr bPL, between about 3500 kg/hr bPL and 35000 kg/hr bPL, between about 3638 kg/hr bPL and 35000 kg/hr

bPL, between about 4000 kg/hr bPL and 35000 kg/hr bPL, between about 5000 kg/hr bPL and 35000 kg/hr bPL, between about 1000 kg/hr bPL and 35000 kg/hr bPL, or between about 20000 kg/hr bPL and 35000 kg/hr bPL. In some embodiments, the post-isolation β-propiolactone product stream includes at least about 30 kmol/hr bPL, at least about 35 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 43 kmol/hr bPL, at least about 45 kmol/hr bPL, at least about 100 kmol/hr bPL, at least about 200 kmol/hr bPL, at least about 300 kmol/hr bPL, or at least about 350 kmol/hr bPL In some embodiments, the mass fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.2-0.24, at least about 0.15, at least about 0.2, or at least about 0.225. In some embodiments, the mole fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.21-0.23, at least about 0.15, at least about 0.2, or at least about 0.22. The post-isolation β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005-0.05, about 0.01-0.04, about 0.044, at most about 0.014, at most about 0.02, or at most about 0.05), unreacted carbon monoxide (in mass fraction of about 0.0005-0.001, at most about 0.001, or at most about 0.002), acetaldehyde (in mass fraction of about 0.0005-0.005, at most about 0.005, or at most about 0.01), succinic anhydride (in mass fraction of about 0.0005-0.0051, at most about 0.005, or at most about 0.01), carbonylation catalyst (in about 0-50 kg/hr, about 0.5-20 kg/hr, about 1-15 kg/hr, about 0-5 kg/hr, about 0.5-2 kg/hr, about 1-1.5 kg/hr, at most 1.4 kg/hr, at most about 2 kg/hr, at most 10 kg/hr, or at most 20 kg/hr), and the remainder solvent. In some variations, the post-isolation β-propiolactone product stream can includes carbonylation catalyst components (in about 0-50 kg/hr, about 0.5-20 kg/hr, about 1-15 kg/hr, about 0-5 kg/hr, about 0.5-2 kg/hr, about 1-1.5 kg/hr, at most 1.4 kg/hr, at most about 2 kg/hr, at most 10 kg/hr, or at most 20 kg/hr).

[0295] In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system can have a temperature of about 20-60°C, about 30-50°C, about 35-45°C, or about 40°C. In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system can have a pressure of about 1-15 bar, about 2-10 bar, or about 7 bar.

Carbonylation Catalyst Regeneration and Accumulation

[0296] The carbonylation catalyst may be recovered from the catalyst recycling system in a form other than as active catalyst. Thus, with reference to FIG. **3**, in some variations, retentate stream **324** may require further processing by one or more additional steps to regenerate the carbonylation catalyst for use in the β-propiolactone production system/production process.

[0297] Further, the carbonylation catalyst (or a component thereof) separated from the β-propiolactone product stream may be accumulated through some interval of time. The accumulated catalyst (or component) forms a spent catalyst batch that is eventually reused (either in whole or in part) in a carbonylation process. The process for which the catalyst is re-used may or may not be the same process from which the catalyst was isolated. Likewise it may be reused for the same process but on another day or in a different reactor. This is in contrast to methods wherein the separated catalyst is treated as a stream within the reaction process which is returned to the reactor within a relatively short period.

[0298] In certain embodiments where the carbonylation catalyst comprises a cationic Lewis acid in combination with an anionic metal carbonyl, the cationic Lewis acid portion of the catalyst is captured from the β-propiolactone product stream without the associated metal carbonyl. In certain embodiments, the cationic Lewis acid is accumulated in a form with a counterion other than the anionic metal carbonyl. In such embodiments, the methods may include a further step of treating the accumulated batch of cationic Lewis acid under conditions

to swap a non-metal carbonyl anion associated with the accumulated Lewis acid with a metal carbonyl anion.

[0299] In certain embodiments where the carbonylation catalyst comprises a cationic Lewis acid in combination with an anionic metal carbonyl, the metal carbonyl portion of the catalyst is captured from the β-propiolactone product stream without the associated Lewis acid. The metal carbonyl thus accumulated may be captured as an anionic metal carbonyl (for example by anion exchange) or it may be accumulated in another form such as a reduced metal species, a metal salt, a neutral metal carbonyl, a mixed metal carbonyl complex, or some other form. In such embodiments, the methods may include a further step of treating the accumulated species to regenerate a catalytically active metal carbonyl compound. In the case where an intact metal carbonyl anion is accumulated (for example by capture on an anion exchange resin), such steps may include metathesis to free the metal carbonyl anion from the resin. This will typically entail flooding the resin with another anion (such as sodium chloride) to displace the metal carbonyl. The metal carbonyl may then be obtained as its sodium salt and utilized to produce active catalyst according to known catalyst synthesis procedures. Therefore, in certain embodiments, systems and methods described herein comprise further steps of freeing accumulated metal carbonyl anion from a resin. In certain embodiments, such steps entail further steps of utilizing accumulated metal carbonyl anion to regenerate active catalyst by combining the accumulated metal carbonyl with a suitable Lewis acid.

[0300] In certain embodiments, the metal carbonyl may be accumulated in a form other than as an intact metal carbonyl anion. For example, in CO-deficient atmospheres, the metal carbonyl may lose one or more CO ligands to form multinuclear metal carbonyl species, salts, or precipitate in elemental form. In other embodiments, a strong ligand may be utilized to displace one or more CO ligands and aid in capture of the metal carbonyl as a new complex. It is known that such species can be utilized to regenerate well defined metal carbonyl compounds

by treatment under CO pressure. Therefore, in certain embodiments, systems and methods described herein include further steps of regenerating the catalytically active metal carbonyl species from a non-catalytically active material accumulated from the β-propiolactone product stream. In certain embodiments, such steps entail further steps of treating accumulated residue derived from a catalytically active metal carbonyl compound under conditions to regenerate a catalytically active metal carbonyl suitable for reuse. In certain embodiments, such steps include a step of treating the accumulated residue under high CO pressure. In certain embodiments, methods include the step of treating a cobalt-containing residue accumulated from the β-propiolactone product stream under conditions of high CO pressure to convert it to dicobalt octacarbonyl.

[0301] In certain embodiments where the accumulation of catalyst separated from the β-propiolactone product stream comprises steps of recovering two or more separate catalyst components in separate recovered catalyst batches, additional steps of recombining recovered catalyst components may be needed to produce active carbonylation catalyst. In some cases the recovered catalyst components may be combined directly while in other steps one or more of the components may require processing as described above prior to step of combining. In certain embodiments such steps entail a metathesis to recombine a recovered cationic Lewis acid with a recovered metal carbonyl anion such as a carbonyl cobaltate.

[0302] The time interval required to accumulate a batch is dependent on the mode of accumulation, and the scale and economics of any processes required to transform the accumulated catalyst residue into active catalyst. In some embodiments, the time interval for accumulation of the catalyst or residue is on the order of hours to days, but may be weeks. Therefore, in certain embodiments of any of the methods described above, the first time interval is in the range from about 1 hour to about 200 hours. In certain embodiments, the first time interval is from about 2 hours to about 8 hours, from about 4 hours to about 16 hours, from

about 12 hours to about 24 hours, or from about 16 hours to about 36 hours. In certain embodiments, the first time interval is from about 1 day to about 20 days, from about 1 day to about 3 days, from about 2 days to about 5 days, from about 5 days to about 10 days, or from about 10 days to about 20 days.

[0303] During this time, the carbonylation reactor may be fed from a reservoir of catalyst which is depleted as the amount of accumulated catalyst (or catalyst residue) increases on the back end of the process. Additional time may be required to process the accumulated catalyst or catalyst residue to remanufacture active catalyst. Therefore, in some variations, some multiple of the first time interval have elapsed from the first time interval when the catalyst was accumulated to the later time at which the carbonylation reactor is fed with a catalyst feed stream containing catalyst derived from the catalyst accumulated during the first time interval. In certain embodiments the length of time between the second time interval (during with catalyst recovered is fed to reactor), and the first time interval (during which the catalyst was accumulated) is on the order of about 1 to about 100 times the length of the first time interval. In other words, if the first time interval is 10 hours, the second time interval would occur from about 10 hours to about 2000 hours after the completion of the accumulation step. In certain embodiments, the length of time between the second time interval and the first time interval is from about 1 to about 10 times the length of the first time interval. In certain embodiments, the length of time between the second time interval and the first time interval is from about 1 to about 3 times, from about 2 to about 5 times, from about 4 to about 10 times, from about 10 to about 50 times, from about 40 to about 80 times, or from about 50 to about 100 times, the length of the first time interval. In certain embodiments, the length of time between the second time interval and the first time interval is greater than 100 times the first time interval.

Continuous Replacement of Catalyst at Predetermined Rate

[0304] In certain variations, the carbonylation catalyst recycling system may be configured to continuously or intermittently introduce to the carbonylation reactor a catalyst replacement component that is different from the carbonylation catalyst (*e.g.*, from the carbonylation catalyst source) and may comprise a species selected from the group consisting of the Lewis acid, a precursor to the Lewis acid, the metal carbonyl, and a precursor to the metal carbonyl.

[0305] In some embodiments, the catalyst replacement component comprises the Lewis acid. In some embodiments, the catalyst replacement component comprises a precursor to the Lewis acid. In some embodiments, the catalyst replacement component comprises the metal carbonyl. In some embodiments, the catalyst replacement component comprises a precursor to the metal carbonyl.

[0306] In some embodiments, the catalyst replacement component is introduced at a rate that results in less than 10% variation in the rate of the carbonylation reaction over a period of one hour. In some embodiments, the catalyst replacement component is introduced at a rate that results in less than 5% variation in the rate of the carbonylation reaction over a period of one hour.

[0307] In some embodiments, the rate at which the catalyst replacement component is added to the carbonylation reactor is determined by the rate at which the carbonylation reaction rate has been observed to decrease. In some embodiments, the rate at which the one or more catalyst replacement components are added to the carbonylation reactor is directly proportional to the rate at which the carbonylation reaction rate has been observed to decrease.

[0308] In some embodiments, the one or more catalyst replacement components are introduced continuously to the carbonylation reactor at the same rate that the carbonylation reaction rate is observed to decrease. In some embodiments, the one or more catalyst replacement components are introduced intermittently to the carbonylation reactor to produce

an average rate which matches the rate at which the carbonylation reaction rate has been observed to decrease.

[0309] Thus, if the carbonylation reaction rate has been observed to decrease 5% over the course of a time period, the catalyst replacement component may either be added continuously or intermittently at such a rate that 5% of the initial amount of Lewis acid or metal carbonyl present in the carbonylation reactor is added over that same time period. In some embodiments, the catalyst replacement component is added continuously. In some embodiments, the catalyst replacement component is added every hour. In some embodiments, the catalyst replacement component is added every 30 minutes. In some embodiments, the catalyst replacement component is added every 15 minutes. In some embodiments, the catalyst replacement component is added every 10 minutes. In some embodiments, the catalyst replacement component is added every 5 minutes. In some embodiments, the catalyst replacement component is added every minute.

[0310] One of skill in the art will appreciate that the shorter the intervals at which the one or more catalyst replacement components are added, the less variation in the overall carbonylation reaction rate will be observed. It should be recognized, however, that this must be balanced against other considerations such as the complexity of making multiple additions.

Recycling to BPL Production system/production process

[0311] In some embodiments, the carbonylation catalyst and/or solvent stream may be recycled to the feed stream or to the carbonylation reactor. In some embodiments, the portion of the solvent and/or catalyst from the β-propiolactone product stream recycled to the carbonylation reactor or feed stream ranges from about 0% to about 100%. In some embodiments, the portion of the solvent and/or catalyst from the β-propiolactone product stream recycled to the carbonylation reactor or feed stream is about 100%, about 90%, about 80%, about 70%, about 60%, about 50%, about 40%, about 30%, about 20%, about 10%, or

about 0%. In some embodiments, a different percentage of the catalyst, as compared to the solvent is recycled, i.e., the proportions of either the catalyst or solvent component do not need to be equal.

BPL Purification System (and Solvent Recycle)

[0312] After the catalyst isolation system, the post-isolation carbonylation stream (i.e., post-isolation β-propiolactone product stream) can be fed to the BPL Purification system. The BPL purification system can separate bPL into a BPL purified stream from low-boiling impurities before it enters the polymerization reaction system, where high purity bPL can be required. In some embodiments, the BPL purified stream can have at least about 90 wt% bPL, at least about 95 wt% bPL, at least about 98 wt% bPL, at least about 99 wt% bPL, at least about 99.3 wt% bPL, at least about 99.5 wt% bPL, at least about 99.8 wt%, or at least about 99.9 wt%. In some embodiments, the BPL purified stream can have at most about 1 wt% solvent, at most about 0.5 wt% solvent, or at most about 0.1 wt% solvent. In some embodiments, the BPL purification system can also create a solvent recycle stream. In some embodiments, the BPL purification system can separate the bPL from the other components in the post-isolation carbonylation stream such as solvent, unreacted ethylene oxide, unreacted carbon monoxide, secondary reaction product acetaldehyde, secondary reaction product succinic anhydride, and carbonylation catalyst or components thereof that was not isolated in the catalyst isolation system. The separation of bPL from the other components in the post-isolation carbonylation stream can be accomplished by various methods known to those of ordinary skill in the art.

[0313] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen

compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0314] In some embodiments, the temperature in the BPL purification system can be at most about 150°C, at most about 125°C, at most about 115°C, at most about 105°C, or at most about 100°C. When bPL is exposed to temperatures greater than 100°C, the bPL can potentially decompose or be partially polymerized. Accordingly, the bPL can be purified without being exposed to temperatures of about 150 °C, 125 °C, 115 °C, 105 °C, or 100 °C.

[0315] In some embodiments, the separation is performed by exploiting the boiling point differential between the beta-propiolactone and the other components of the carbonylation product stream, primarily the solvent. In some embodiments, the boiling point of the solvent is lower than the boiling point of the beta-propiolactone. In some embodiments, the solvent is volatilized (e.g., evaporated) from the BPL purification feed along with other lighter components (e.g., ethylene oxide & acetaldehyde), leaving behind bPL, other heavier compounds (e.g., catalyst and succinic anhydride) and some leftover solvent from the BPL purification feed. In some embodiments, this includes exposing the BPL purification feed to reduced pressure. In some embodiments, this includes exposing BPL purification feed to increased temperature. In some embodiments, this includes exposing the BPL purification feed to both reduced pressure and increased temperature.

[0316] In some embodiments, the pressure is selected so that the boiling point of the solvent is reduced by about 5 °C as compared to the boiling point at atmospheric pressure. In some embodiments, the pressure is selected so the boiling point of the solvent is reduced by about 10 °C as compared to the boiling point at atmospheric pressure. In some embodiments, the pressure is selected so the boiling point of the solvent is reduced by about 20 °C as compared to the boiling point at atmospheric pressure. In some embodiments, the pressure is selected so

the boiling point of the solvent is reduced by about 50 °C as compared to the boiling point at atmospheric pressure.

[0317] In some embodiments, the increased temperature is above the boiling point of the solvent but below the boiling point of the beta-propiolactone, at the selected pressure. In some embodiments, the temperature is at least about 20 °C below the boiling point of the beta-propiolactone. In some embodiments, the temperature is at least about 30 °C below the boiling point of the beta-propiolactone. In some embodiments, the temperature is at least about 50 °C below the boiling point of the beta-propiolactone.

[0318] In some embodiments, the reduced pressure is in the range from about 1 Torr to about 760 Torr. In some embodiments, the pressure is in the range of about 1 Torr to about 400 Torr. In some embodiments, the pressure is in the range of about 5 Torr to about 200 Torr. In some embodiments, the pressure is in the range of about 10 Torr to about 100 Torr. In some embodiments, the pressure is in the range of about 20 Torr to about 50 Torr. In some embodiments, the pressure is about 50 Torr, about 100 Torr, about 150 Torr, about 200 Torr, about 250 Torr, about 300 Torr, about 400 Torr about 500 Torr, about 600 Torr or about 700 Torr.

[0319] In some embodiments, the separation step is performed at a pressure below about 100 Torr and at a temperature above about 120 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 100 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 50 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 110 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 90 °C. In some embodiments, the separation step is performed at a pressure below about

20 Torr and at a temperature above about 60 °C. In some embodiments, the separation step is performed at a pressure below about 10 Torr and at a temperature above about 50 °C.

[0320] In some embodiments, the separation may be effected in a sequence of steps, each operating at an independent temperature and pressure. For example, in one embodiment, two steps may be used to obtain a more effective separation of beta-propiolactone, or a separate separation step may be used to isolate certain reaction by-products. In some embodiments, when a mixture of solvents is used, multiple separation steps may be required to remove particular solvents, individually or as a group, and effectively isolate the beta-propiolactone.

[0321] In certain embodiments, the separation of the beta-propiolactone from the BPL purification feed is performed in two stages. In some embodiments the process includes a preliminary separation step to remove one or more components of the BPL purification feed having boiling points below that of the beta-propiolactone product.

[0322] In some embodiments, the preliminary separation step includes separating the BPL purification feed into a gas stream comprising ethylene oxide, solvent, and bPL (and potentially carbon monoxide, acetaldehyde, and/or bPL); and a liquid stream comprising beta-propiolactone, carbonylation catalyst (and potentially succinic anhydride and/or solvent). In the second step of separation, the liquid stream is further separated into a beta-propiolactone stream comprising beta-propiolactone, a solvent stream comprising solvent, and potentially a catalyst and succinic anhydride purge stream. The gas stream can also be further separated into a solvent stream comprising solvent, a light gases stream comprising solvent and ethylene oxide (and potentially acetaldehyde), and a liquid bPL stream comprising bPL and solvent. The liquid bPL stream can join with the liquid stream prior to separation of the liquid stream and form a combined feed to the second separation step. In some embodiments, the solvent stream from the second separation step and/or the solvent stream from the gas stream separation

can form the solvent recycle stream which can be fed to the carbonylation reaction system or to a solvent reservoir.

[0323] In some embodiments where one or more solvents with a boiling point lower than that of the beta-propiolactone are present, the lower boiling solvent may be volatilized (e.g., evaporated) from the BPL purification feed in a preliminary separation step, leaving behind a mixture comprising catalyst, beta-propiolactone, other solvents (if any) and other compounds in the BPL purification stream which is then further treated to separate the beta-propiolactone stream.

[0324] In certain embodiments where the separation is performed in two stages, the first step of separation comprises exposing the reaction stream to mildly reduced pressure to produce the gas stream and the liquid stream. In certain embodiments where the separation is performed in two stages, the gas stream can be returned to the carbonylation step.

[0325] In certain embodiments, the separation of the beta-propiolactone from the BPL purification feed is performed in three stages. In the first step of separation, the BPL purification feed is separated into a gaseous stream comprising ethylene oxide, solvent, and bPL (and potentially carbon monoxide and/or acetalhydride); and a liquid stream comprising solvent, beta-propiolactone, and carbonylation catalyst (and potentially succinic anhydride). In the second step of separation, the gaseous stream is separated into a solvent side stream comprising solvent; a light gas stream comprising ethylene oxide and solvent (and potentially carbon monoxide and/or acetaldehyde); and second liquid stream comprising solvent and bPL. In the third step of separation, the second liquid stream and the first liquid stream are combined and separated into a gaseous solvent stream comprising solvent, a purified BPL stream comprising bPL, and potentially a catalyst and succinic anhydride purge stream. In some embodiments, the solvent side stream and/or the gaseous solvent stream can be used as the

solvent recycle stream for use in the carbonylation reaction system or can be stored in a solvent storage tank.

[0326] In certain embodiments where the separation is performed in three stages, the first step of separation comprises exposing the BPL purification feed to atmospheric pressure. In certain embodiments where the separation is performed in three stages, the second step of separation comprises exposing the gaseous stream to atmospheric pressure. In certain embodiments where the separation is performed in three stages, the third step of separation comprises exposing the gaseous stream to a vacuum or reduced pressure. In certain embodiments, the reduced pressure is between about 0.05-0.25 bara. In certain embodiments, the reduced pressure is between about 0.1-0.2 bara or about 0.15 bara.

[0327] In certain embodiments, the separation of the beta-propiolactone from the BPL purification feed is performed in four stages. In the first step of separation, the BPL purification feed is separated into a gaseous stream comprising ethylene oxide, solvent, and bPL (and potentially carbon monoxide and/or acetalhydride); and a liquid stream comprising solvent, beta-propiolactone, and carbonylation catalyst (and potentially succinic anhydride). In the second step of separation, the gaseous stream is separated into a solvent side stream comprising solvent; a light gas stream comprising ethylene oxide and solvent (and potentially carbon monoxide and/or acetaldehyde); and second liquid stream comprising solvent and bPL. In the third step of separation, the second liquid stream and the first liquid stream are combined and separated into a gaseous solvent stream comprising solvent, a purified BPL stream comprising bPL, and potentially a catalyst and succinic anhydride purge stream. In the fourth step of separation, the light gas stream is separated into a third solvent stream comprising solvent and a second light gas stream comprising ethylene oxide (and potentially carbon monoxide and/or acetaldehyde). In some embodiments, the solvent side stream, the gaseous solvent stream,

and/or the third solvent stream can be used as the solvent recycle stream for use in the carbonylation reaction system or can be stored in a solvent storage tank.

[0328] In certain embodiments where the separation is performed in four stages, the first step of separation comprises exposing the BPL purification feed to atmospheric pressure. In certain embodiments where the separation is performed in four stages, the second step of separation comprises exposing the gaseous stream to atmospheric pressure. In certain embodiments where the separation is performed in four stages, the third step of separation comprises exposing the combined liquid stream to a vacuum or reduced pressure. In certain embodiments, the reduced pressure is between about 0.05-0.25 bara. In certain embodiments, the reduced pressure is between about 0.1-0.2 bara or about 0.15 bara. In certain embodiments where the separation is performed in four stages, the fourth step of separation comprises exposing the light gas stream to atmospheric pressure.

[0329] In some embodiments, the BPL purification system can include at least one distillation column to separate bPL from the other components in the post-isolation carbonylation stream. In some embodiments, the BPL purification system includes at least two distillation columns. In some embodiments, the BPL purification system includes at least three distillation columns. In some embodiments, at least one of the distillation columns is a stripping column (i.e., stripper). In some embodiments, at least one of the distillation columns is a vacuum column. In some embodiments, the BPL purification system can include an initial evaporator, wherein the post-isolation carbonylation stream is first fed to an evaporator in the BPL purification system. The evaporator can perform a simple separation between the solvent and the bPL in the post-isolation carbonylation stream. The evaporator can reduce loads on subsequent distillation columns making them smaller. In some embodiments, the evaporator can reduce loads on subsequent distillation columns making them smaller by evaporating

solvent in the post-isolation carbonylation stream at about atmospheric pressure and about 100°C.

[0330] FIG. **16** illustrates an exemplary embodiment of the BPL Purification system disclosed herein.

Feed Stream

[0331] As depicted in FIG. **16**, in some embodiments of the exemplary system, feed **1616** to BPL purification system **1617** can be the post-isolation carbonylation product stream (i.e., post-isolation β-propiolactone product stream). In other embodiments, the feed to the BPL purification system can be the carbonylation product stream. In some embodiments, the feed to BPL purification system is at least about 10000 kg/hr, at least about 11000 kg/hr, at least about 12000 kg/hr, at least about 13000 kg/hr, at least about 13777 kg/hr, at least about 20000 kg/hr, at least about 50000 kg/hr, at least about 100000 kg/hr, at least about 110000 kg/hr, at least about 120000 kg/hr, at least about 130000 kg/hr, or at least about 137770 kg/hr. In some embodiments, the feed to BPL purification system is about 10000 kg/hr, about 11000 kg/hr, about 12000 kg/hr, about 13000 kg/hr, about 13777 kg/hr, about 20000 kg/hr, about 50000 kg/hr, about 100000 kg/hr, about 110000 kg/hr, about 120000 kg/hr, about 130000 kg/hr, or about 137770 kg/hr. In some embodiments, the feed to BPL purification system is between about 10000 kg/hr and about 13777 kg/hr, between about 11000 kg/hr and about 13777 kg/hr, between about 12000 kg/hr and about 13777 kg/hr, between about 13000 kg/hr and about 13777 kg/hr, between about 10000 kg/hr and 137770 kg/hr, between about 11000 kg/hr and about 137770 kg/hr, between about 12000 kg/hr and about 137770 kg/hr, between about 13000 kg/hr and about 137770 kg/hr, between about 13777 kg/hr and about 137770 kg/hr, between about 20000 kg/hr and about 137770 kg/hr, between about 50000 kg/hr and about 137770 kg/hr, between about 100000 kg/hr and about 137770 kg/hr, between about 110000 kg/hr and about 137770 kg/hr, between about 120000 kg/hr and about 137770 kg/hr, or between about

130000 kg/hr and about 137770 kg/hr. In some embodiments, the feed to BPL purification system has a bPL wt% between about 10-30, about 15-28, about 18-25, about 20-25, about 22-23, about 22.5, or at least 22.5. In some embodiments, the feed to BPL purification system has solvent (e.g., THF) wt% between 60-90, about 65-85, about 70-80, about 72-78, about 74-76, about 75, about 75.8, or at least about 75. In some embodiments, the feed to BPL purification system has a CO wt% between about 0-0.2, about 0.05-0.15, about 0.1, or at most about 0.2. In some embodiments, the feed to BPL purification system has an acetaldehyde wt. % between about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2. In some embodiments, the feed to BPL purification system has a succinic anhydride wt. % between about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2. In some embodiments, the feed to BPL purification system has an EO wt% between about 0-3, about 0.5-2, about 1-2, about 1.4, at most about 1.4, or at most about 2. In some embodiments, the feed to the BPL purification system has trace amounts of carbonylation catalyst. In some embodiments, the feed to the BPL purification system has trace amounts of carbonylation catalyst components.

Evaporator

[0332] In some embodiments, the feed to the BPL purification system can be fed to evaporator **1628**. In some embodiments, the evaporator can operate at most about 5 bara, at most about 4 bara, at most about 3 bara, at most about 2 bara, at most about atmospheric pressure (i.e., 1 bara), or at about atmospheric pressure. In some embodiments, the evaporator can operate at a temperature between about 80-120°C, between about 90-100°C, between about 95-105°C, at about 100°C, at most about 100°C, at most about 105°C, at most about 110°C, or at most about 120°C. In some embodiments, the evaporator is a flash tank. Referring again to FIG. **16**, in the exemplary system evaporator **1628** can separate the feed into overhead stream **1629** and bottoms stream 1630. Overhead stream **1629** can comprise mainly of THF with low

boiling point components (e.g., CO, EO, acetaldehyde) and a small amount of bPL. In some embodiments, overhead stream **1629** can have a mass flow rate of at least about 9000 kg/hr, at least about 10000 kg/hr, at least about 11000 kg/hr, at least about 11500 kg/hr, or at least about 12000 kg/hr. In some embodiments, overhead stream 1629 can have a solvent (e.g., THF) wt% of about 75-95, about 80-90, about 85, about 86.7, at least about 75, at least about 80, at least about 85, or at least about 90. In some embodiments, overhead stream 1629 can have a bPL wt% of about 0-20, about 5-20, about 8-15, about 10, about 11.5, at most about 25, at most about 20, at most about 15, at most about 11.5, at most about 10, or at most about 5. In some embodiments, overhead stream 1629 can have a carbon monoxide wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.2, or at most about 0.1. In some embodiments, overhead stream 1629 can have an ethylene oxide wt% of about 0-5, about 0.5-3, about 1-2, about 1.6, at most 5, at most 3, at most 2, at most 1.6. In some embodiments, overhead stream 1629 can have an acetaldehyde wt% of about 0-0.4, about 0.1-0.3, about 0.2, at most about 0.4, or at most about 0.2.

[0333] In some embodiments, bottoms stream **1630** can have a mass flow rate of at least about 500 kg/hr, at least about 1000 kg/hr, at least about 1500 kg/hr, at least about 2000 kg/hr, at least about 2200 kg/hr, at least about 3000 kg/hr, at least about 4000 kg/hr, at least about 5000 kg/hr, at least about 10000 kg/hr, at least about 15000 kg/hr, at least about 20000 kg/hr, at least about 22000 kg/hr, at least about 30000 kg/hr. In some embodiments, bottoms stream 1630 can have a mass flow rate of between about 500 kg/hr and about 3000 kg/hr, between about 1000 kg/hr and about 3000 kg/hr, between about 1500 kg/hr and about 3000 kg/hr, between about 2000 kg/hr and about 3000 kg/hr, between about 2200 kg/hr and about 3000 kg/hr, between about 500 kg/hr and about 30000 kg/hr, between about 1000 kg/hr and about 30000 kg/hr, between about 1500 kg/hr and about 30000 kg/hr, between about 2000 kg/hr and about 30000 kg/hr, between about 2200 kg/hr and about 30000 kg/hr, between about 3000

kg/hr and about 30000 kg/hr, between about 4000 kg/hr and about 30000 kg/hr, between about 5000 kg/hr and about 30000 kg/hr, between about 10000 kg/hr and about 30000 kg/hr, between about 15000 kg/hr and about 30000 kg/hr, between about 20000 kg/hr and about 30000 kg/hr, between about 22000 kg/hr and about 30000 kg/hr. In some embodiments, bottoms stream 1630 can have a bPL wt% of about 60-95, about 65-90, about 70-85, about 75-85, about 79.7, about 80, at least about 65, at least about 70, at least about 75, at least about 79.7, at least about 85. In some embodiments, bottoms stream 1630 can have a solvent wt% of about 5-40, about 10-30, about 15-25, about 18-20, about 19.2, about 20, at most 40, at most 30, at most 25, at most 20, at most 19.2, at most 15, or at most 10. In some embodiments, bottoms stream 1630 can have an ethylene oxide wt% of about 0-0.4, about 0.1-0.3, about 0.2, at most about 0.4, or at most about 0.2. In some embodiments, bottoms stream 1630 can have a succinic anhydride wt% of about 0-2, about 0.2-1.6, about 0.4-1.2, about 0.6-1, about 0.7-0.9, at most about 2, at most about 1, at most about 0.8. In some embodiments, the bottoms stream 1630 can have a carbonylation catalyst wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.2, or at most about 0.1. In some embodiments, the bottoms stream 1630 can have a carbonylation catalyst component wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.2, or at most about 0.1.

Solvent Purification Column

[0334] Referring again to FIG. **16**, in the exemplary system depicted overhead stream **1629** can be sent to solvent purification column **1631**. The solvent purification column can be a distillation column. In some embodiments, the solvent purification column can be a stripping column or stripper. In some embodiments, the solvent purification column can operate at most about 5 bara, at most about 4 bara, at most about 3 bara, at most about 2 bara, at most about atmospheric pressure (i.e., 1 bara), or at about atmospheric pressure. In some embodiments, the evaporator can operate at a temperature of at most about 100°C, at most about 105°C, at

most about 110°C, or at most about 120°C. In some embodiments, an overhead temperature is maintained at about 20-60°C, about 30-50°C, about 40-50°C, about 44°C. In some embodiments, the solvent purification column can prevent bPL from getting into any vent streams. In some embodiments, solvent purification column can have at least 12 stages with a condenser as stage 1. In some embodiments, solvent purification column can have an internal cooler which can create a side stream. In some embodiments, solvent purification column can have an internal cooler above the side stream withdrawal. In some embodiments, internal cooler can be between stages in the middle of the column. In some embodiments, internal cooler can be between stages 5 and 6 of the solvent purification column. In some embodiments, solvent purification column can separate overhead stream **1629** into overhead stream **1632**, bottoms stream **1634**, and side stream **1633**. Overhead stream **1632** can comprise low boiling components (e.g., EO, CO, acetaldehyde) and around half solvent. Bottoms stream **1634** can comprise mainly bPL and solvent. In some embodiments, solvent purification column can recover at least 90wt%, at least 95wt%, at least 98wt%, at least 99wt%, or at least 99.5wt% of bPL from overhead stream 1629 in bottoms stream 1634.

[0335] In some embodiments, overhead stream **1632** can have a mass flowrate of at least 200 kg/hr, at least 300 kg/hr, at least 400 kg/hr, at least 411 kg/hr, at least 500 kg/hr, at least 1000 kg/hr, at least 1500 kg/hr, at least 2000 kg/hr, at least 3000 kg/hr, at least 4000 kg/hr, at least 4110 kg/hr, or at least 5000 kg/hr. In some embodiments, overhead stream **1632** can have a mass flowrate of between 200 kg/hr and 500 kg/hr, between 300 kg/hr and 500 kg/hr, between 400 kg/hr and 500 kg/hr, between 411 kg/hr and 500 kgr/hr, between 200 kg/hr and 5000 kg/hr, between 300 kg/hr and 5000 kg/hr, between 400 kg/hr and 5000 kg/hr, between 411 kg/hr and 5000 kgr/hr. In some embodiments, overhead stream 1632 can have a solvent (e.g., THF) wt% of about 30-70, about 40-60, about 45-55, about 50-55, about 50, about 53.9, at most 75, at most 65, at most 60, at most 55, at most 53.9, at most 50, at most 45. In some embodiments,

overhead stream 1632 can have an ethylene oxide wt% of about 20-60, about 30-50, about 35-45, about 37-43, about 40.6, at least about 20, at least about 25, at least about 30, at least about 35, at least about 40, at least about 40.6, at least about 45, or at least about 50. In some embodiments, overhead stream 1632 can have a carbon monoxide wt% of about 0-5, about 0.5-3, about 1-2, about 1.5-2, about 1.7, at most about 5, at most about 3, at most about 2, at most about 1.7, at most about 1. In some embodiments, overhead stream 1632 can have a acetaldehyde wt% of about 0-10, about 1-7, about 2-5, about 3-4.5, about 3.5-4, about 3.8, at most about 10, at most about 7, at most about 5, at most about 4, at most about 3.8, at most about 3.

[0336] In some embodiments, bottoms stream **1634** can have a mass flowrate of at least about 1000 kg/hr, at least about 1200 kg/hr, at least about 1400 kg/hr, at least about 1600 kg/hr, at least about 1643 kg/hr, at least about 1800 kg/hr, at least about 4000 kg/hr, at least about 7500 kg/hr, at least about 10000 kg/hr, at least about 12000 kg/hr, at least about 14000 kg/hr, at least about 16000 kg/hr, at least about 16430 kg/hr, or at least about 18000 kg/hr. In some embodiments, bottoms stream 1634 can have a mass flowrate of about 1000 kg/hr, about 1200 kg/hr, about 1400 kg/hr, about 1600 kg/hr, about 1643 kg/hr, about 1800 kg/hr, about 4000 kg/hr, about 7500 kg/hr, about 10000 kg/hr, about 12000 kg/hr, about 14000 kg/hr, about 16000 kg/hr, about 16430 kg/hr, or about 18000 kg/hr. In some embodiments, bottoms stream 1634 can have a mass flowrate of between 1000 kg/hr and 1800 kg/hr, between 1200 kg/hr and 1800 kg/hr, between 1400 kg/hr and 1800 kg/hr, between 1600 kg/hr and 1800 kg/hr, between 1643 kg/hr and 1800 kg/hr, between 1000 kg/hr and 18000 kg/hr, between 1200 kg/hr and 18000 kg/hr, between 14000 kg/hr and 18000 kg/hr, between 16000 kg/hr and 18000 kg/hr, between 1643 kg/hr and 18000 kg/hr, between 4000 kg/hr and 18000 kg/hr, between 10000 kg/hr and 18000 kg/hr, or between 16000 kg/hr and 18000 kg/hr. In some embodiments, bottoms stream 1634 can have a bPL wt% of about 60-95, about 70-90, about 75-85, about 80, about 80.4, at

least 60, at least 70, at least 75, at least 80, at least 80.4, at least 85, at least 90, or at least 95. In some embodiments, bottoms stream 1634 can have a solvent wt% of about 5-40, about 10-30, about 15-25, about 20, about 19.5, at most 40, at most 30, at most 25, at most 20, at most 19.5, at most 15, or at most 10. In some embodiments, bottoms stream 1634 can have an ethylene oxide wt% of about 0-0.4, about 0.1-0.3, about 0.2, at most about 0.4, or at most about 0.2.

[0337] In some embodiments, side stream **1633** can have a mass flow rate of at least about 6000 kg/hr, at least about 7000 kg/hr, at least about 8000 kg/hr, at least about 9000 kg/hr, at least about 9500 kg/hr, at least about 9508 kg/hr, at least about 10000 kg/hr, at least about 20000 kg/hr, at least about 40000 kg/hr, at least about 60000 kg/hr, at least about 70000 kg/hr, at least about 80000 kg/hr, at least about 90000 kg/hr, at least about 95000 kg/hr, at least about 95080 kg/hr, or at least about 100000 kg/hr. In some embodiments, side stream 1633 can have a mass flow rate of about 6000 kg/hr, about 7000 kg/hr, about 8000 kg/hr, about 9000 kg/hr, about 9500 kg/hr, about 9508 kg/hr, about 10000 kg/hr, about 20000 kg/hr, about 40000 kg/hr, about 60000 kg/hr, about 70000 kg/hr, about 80000 kg/hr, about 90000 kg/hr, about 95000 kg/hr, about 95080 kg/hr, or about 100000 kg/hr. In some embodiments, side stream 1633 can have a mass flow rate of between 6000 kg/hr and 10000 kg/hr, between 7000 kg/hr and 10000 kg/hr, between 8000 kg/hr and 10000 kg/hr, between 9000 kg/hr and 10000 kg/hr, between 9500 kg/hr and 10000 kg/hr, between 9508 kg/hr and 10000 kg/hr, between 6000 kg/hr and 100000 kg/hr, between 10000 kg/hr and 100000 kg/hr, between 20000 kg/hr and 100000 kg/hr, between 40000 kg/hr and 100000 kg/hr, between 60000 kg/hr and 100000 kg/hr, between 70000 kg/hr and 100000 kg/hr, between 80000 kg/hr and 100000 kg/hr, or between 90000 kg/hr and 100000 kg/hr, between. In some embodiments, side stream 1633 can have a solvent wt% of at least 95, at least 98, at least 99, at least 99.7. In some embodiments, side stream 1633 can have an ethylene oxide wt. % of about 0-0.4, about 0.1-0.3, about 0.2, at most about

0.4, or at most about 0.2. In some embodiments, side stream 1633 can have a bPL wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2.

BPL Purification Column

[0338] Bottoms stream **1630** and bottoms stream **1634** can be combined and sent to BPL purification column **1635**. BPL purification column can be a distillation column. In some embodiments, BPL purification column can be a vacuum column or a column operating under reduced pressure. In some embodiments, the operating pressure of the BPL purification column can be less than atmospheric pressure (1 bara), less than about 0.5 bara, less than about 0.25 bara less than 0.2 bara, less than 0.15 bara, or about 0.15 bara. In some embodiments, the BPL purification column can include a reboiler that can be maintained at most about 120°C, at most about 110°C, at most about 100°C, or about 100°C. In some embodiments, an overhead temperature is maintained at about 5-30°C, about 10-20°C, about 12-16°C, about 14°C.

[0339] In some embodiments, BPL purification column can separate the combined bottoms streams **1630** and **1634** into overhead stream **1636** and bottoms stream 1618 (i.e., BPL purified stream **1618**). Bottoms stream **1618** can be substantially pure bPL with minimal solvent. In some embodiments, bottoms stream **1618** can also include some heavy components such as residual carbonylation catalyst and succinic anhydride. The carbonylation catalyst can be considered to be non-volatile and can accumulate in the BPL purification column's sump. Accumulated catalyst can be removed periodically by purging sump when the catalyst wt% reaches a predefined value (e.g., at least 1wt%, 2wt%, 3wt%, 4wt%, or 5wt%). In contrast to the carbonylation catalyst, succinic anhydride can have some volatility and if accumulated in the sump can produce an undesirable rise in boiling temperature in the reboiler. In some embodiments, succinic anhydride can also accumulate in the sump and can be purged in the same manner the accumulated catalyst can be purged. In some embodiments, overhead stream 1636 can have a mass flow rate of about at least about 500 kg/hr, at least about 600 kg/hr, at

least about 700 kg/hr, at least about 750 kg/hr at least about 800 kg/hr, or at least about 850 kg/hr. In some embodiments, overhead stream 1636 can have a solvent wt% of at least about 95, at least about 98, at least about 99, at least about 99.1, or at least about 99.5. In some embodiments, overhead stream 1636 can have an ethylene oxide wt% of about 0-3, about 0.2-2, about 0.2-1.5, about 0.5-1, about 0.8, at most about 3, at most about 2, at most about 1, at most about 0.8, at most about 0.5. In some embodiments, overhead stream 1638 can have an acetaldehyde wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2.

[0340] In some embodiments, bottoms stream **1618** can have a mass flow rate of at least about 1000 kg/hr, at least about 2000 kg/hr, at least about 2500 kg/hr, at least about 3000 kg/hr, at least about 3100 kg/hr, at least about 3500 kg/hr, at least about 4000 kg/hr, at least about 5000 kg/hr, at least about 1000 kg/hr, at least about 20000 kg/hr, at least about 35000 kg/hr, at least about 36380 kg/hr, or at least about 40000 kg/hr. In some embodiments, bottoms stream 1618 can have a mass flow rate of about 2000 kg/hr, about 2500 kg/hr, about 3000 kg/hr, about 3500 kg/hr, about 3638 kg/hr, about 4000 kg/hr, about 5000 kg/hr, about 1000 kg/hr, about 20000 kg/hr, about 35000 kg/hr, about 36380 kg/hr, or about 40000 kg/hr. In some embodiments, bottoms stream 1618 can have a mass flow rate of between 1000 kg/hr and 4000 kg/hr, or between 1000 kg/hr and 40000 kg/hr. In some embodiments, bottoms stream 1618 can have a bPL wt% of at least about 95, at least about 98, at least about 99, at least about 99.3, or at least about 99.5. In some embodiments, bottoms stream 1618 can have a solvent wt. % of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2. In some embodiments, bottoms stream 1618 can have a succinic anhydride wt% of about 0-3, about 0.1-2, about 0.2-1, about 0.5-1, about 0.6, at most about 3, at most about 2, at most about 1, at most about 0.6, at most about 0.5. In some embodiments, bottoms stream 1618 can have trace amounts of carbonylation catalyst. In some embodiments, BPL purification column can have

a purge for the carbonylation catalyst and/or succinic anhydride in the bottoms stream **1618**. In some embodiments, the purge can be a valve.

Light Gas Column

[0341] Overhead stream **1632** can be sent to light gas column **1637** to be separated into overhead stream **1639** and bottoms stream **1638**. The light gas column can be a distillation column. In some embodiments, the light gas column can operate at most about 5 bara, at most about 4 bara, at most about 3 bara, at most about 2 bara, at most about atmospheric pressure (i.e., 1 bara), or at about atmospheric pressure. In some embodiments, light gas column can include a partial condenser. In some embodiments, the partial condenser operates at a temperature of at about 0-20°C, about 5-15°C, about 10-15 °C, about 10-13 °C. In some embodiments, the temperature maintained at the bottom of light gas column is about 20-70°C, about 40-60°C, about 45-55°C, or about 50°C. In some embodiments, the overhead temperature maintained in light gas column can be about -10-10°C, about -5-5°C, about -2-3°C, or about 1 °C. Overhead stream 1639 can comprise mostly of the acetaldehyde produced in the carbonylation reaction system as well as low boiling point ethylene oxide. In some embodiments, overhead stream 1639 can be disposed of (e.g., incinerator, flare, etc.) so acetaldehyde does not accumulate in the overall production system/production process.

[0342] In some embodiments, overhead stream **1639** can have a mass flow rate of about 50 kg/hr, about 100 kg/hr, about 150 kg/hr, about 175 kg/hr, about 200 kg/hr, about 250 kg/hr, at least 500 kg/hr, at least 1000 kg/hr, at least 1500 kg/hr, at least 2000 kg/hr, or at least 2500 kg/hr. In some embodiments, overhead stream 1639 can have a mass flow rate of between 50 kg/hr and 250 kg/hr, between 100 kg/hr and 250 kg/hr, between 200 kg/hr and 250 kg/hr, or between 50 kg/hr and 2000 kg/hr. In some embodiments, overhead stream 1639 can have an ethylene oxide wt% of at least about 70, at least about 75, at least about 80, at least about 85, at least about 89.5, at least about 90, or at least about 95. In some embodiments, overhead

stream 1639 can have an acetaldehyde wt% of about 0-15, about 1-10, about 2-8, about 6.1, at most about 15, at most about 10, at most about 6.1, at most about 5, or at most about 2. In some embodiments, overhead stream 1639 can have a carbon monoxide wt% of about 0-12, about 1-10, about 2-6, about 4.10, at most about 12, at most about 10, at most about 6, at most about 5, at most about 4.1, or at most about 2. In some embodiments, overhead stream 1639 can have a solvent wt. % of about 0-2, about 0.1-1, about 0.2-0.6, about 0.4, at most about 2, at most about 1, at most about 0.5, at most about 0.4, or at most about 0.2.

[0343] In some embodiments, bottoms stream **1638** can have a mass flow rate of about 50 kg/hr, about 150 kg/hr, about 200 kg/hr, about 235 kg/hr, about 250 kg/hr, about 300 kg/hr or about 350 kg/hr. In some embodiments, bottoms stream 1638 has a solvent wt% of at least about 75, at least about 80, at least about 85, at least about 90, at least about 93.9, at least about 95, at least about 98, or at least about 99. In some embodiments, bottoms stream 1638 has an ethylene oxide wt% of about 0-12, about 1-10, about 2-6, about 4, at most about 12, at most about 10, at most about 8, at most about 5, at most about 4, or at most about 2. In some embodiments, bottoms stream 1638 has an acetaldehyde wt% of about 0-10, about 0.5-5, about 1-4, about 1-3, about 2.2, at most about 10, at most about 5, at most about 2.2, at most about 2, at most about 1.

Solvent Recycle Stream

[0344] In some embodiments, side stream **1633**, bottoms stream **1638**, overhead stream **1636** or combinations thereof can form solvent recycle stream **1623**. In some embodiments, side stream **1633**, bottoms stream **1638**, and overhead stream **1636** can be combined to form solvent recycle stream **1623**. In some embodiment, side stream **1633**, bottoms stream **1638**, and/or overhead stream **1636** can be sent to a solvent recycle tank or storage. In some embodiments, the solvent recycle stream is fed back to the carbonylation reaction system. In some embodiments, the solvent recycle stream fed to the carbonylation reaction system is from

the solvent recycle tank or storage. In some embodiments, the solvent streams entering and/or exiting the solvent recycle tank or storage can be purified for example by passing the stream through an absorber to remove potential oxygen and/or moisture from the stream. In some embodiments, the solvent recycle tank or storage can be equipped with sensors to determine the water and/or oxygen content in the storage tank.

Preferred Distillation System

[0345] In preferred embodiment, distillation sub-system consists of 3 distillation columns: (1) Lights Removal column, (2) THF Solvent Recovery column, and (3) bPL Purification column.

1. Lights Revmoval Column

[0346] The purpose of this column is to recover Ethylene Oxide (EO) for recycle back to the Carbonylation Reactor as well as to separate low-boiling impurities such as Acetaldehyde (ACH). Distillate stream from this column may contain THF, EO, ACH or only EO and ACH. This colomn receives a permeate stream from a carbonylation catalyst recovery zone and in a highly preferred form has the following component with representativie compositions of THF (about 75.2 wt%), bPL (about 20.5wt%), Ethylene Oxide (about 4.1wt%), Acetaldehyde (about 0.07wt%), Succinic Anhydride (about 0.02wt%), traces of low and high boiling impurities, and trace residual carbonylation catalyst is fed to Lights Removal distillation column. The distillation column is operated at the pressure of about 1.3 bara (column is operated at atmospheric pressure or slightly above atmospheric pressure). The reboiler temperature is maintained at or below 105°C. Lights column distillate stream consisting essentially of THF (about 93.4wt%), EO (about 6.5wt%), ACH (0.1wt%), and traces of low boiling impurities is fed back to the carbonylation reactor or to optional ACH removal system. The lights column in a a highly preferred form produces a bottoms stream consisting essentially of bPL (about 54.9wt%), THF (about 45.0wt%), Succinic Anhydride (about 0.05wt%), trace amounts of low-

and high-boiling impurities, and trace residual carbonylation catalyst and high-boiling impurities is fed forward to THF Solvent Recovery column (2).

[0347] In some embodiments Lights Removal column can be operated in such a way that Distillate stream consists of only Ethylene Oxide and Acetaldehyde and all THF is exiting the column with the Bottoms stream. If the lights removal column is operated in this configuration the distillate consists essentially of EO (about 98.8wt%), ACH (about 1.2wt%), and trace of low boiling impurities. The bottoms stream in this column configuration consists essentially of THF (about 78.5wt%), bPL (about 21.5wt%), SAH (about 0.02wt%), trace amounts of residual carbonylation catalyst, trace amounts of low- and high-boiling impurities.

[0348] Accumulation of Acetaldehyde within carbonylation/distillation system can be avoided by implementing a small purge from distillate stream or removed from the distillate stream using an absorbent such as molecular sieves (non-limiting examples are Molecular Sieve 3A, 4A, 5A, 13X, etc.). Optionally, ACH is separated from EO using distillation or extractive distillation.

2. THF Solvent Recovery Column

[0349] The purpose of this column is to recover THF solvent for recycle back to the carbonylation reactor. Due to the high boiling point of bPL (162°C at atmospheric pressure) this column is operated at pressures below atmospheric to limit the reboiler temperature below 105°C and avoid autopolymerization of bPL. Distillate stream from this column contains essentially pure THF and bottoms stream of this column contains bPL, SAH, residual carbonylation catalyst, and trace amounts of high boiling impurities.

[0350] Lights Column Bottom stream containing THF, bPL, SAH, residual carbonylation catalyst, and trace amounts of low and high boiling impurities is fed to THF Solvent Recovery distillation column (the composition of this stream is presented in the section above).

Optionally, the THF solvent make-up stream may be fed to this column – this allows removal of O2, H2O, and BHT inhibitor from make-up THF.

[0351] The distillation column is operated at the absolute pressure of about 100 Torrs (column is operated under vacuum) and the reboiler temperature is maintained at or below 105°C. The column is designed to minimize air intrusion into the column simplifying removal of O2 and H2O contaminants from recycled THF Solvent stream in downstream unit operation.

[0352] The distillate stream from this column consisting of essentially pure THF (purity greater than 99.9wt%) with trace amounts of low- and high-boiling impurities is recycled back to the carbonylation reactor. Optionally and before it is recycled, this stream may be passed through purification system for removal of contaminants such as O2 and H2O. These impurities can be removed by any means known in the art such as absorption, adsorption, extractive distillation, azeotropic distillation, etc.

[0353] The bottoms stream consists of bPL (about 99.8wt%), SAH (about 0.1 wt%), small amounts of residual carbonylation catalyst, and traces of low- and high-boiling impurities. This stream is fed forward to bPL Purification column.

3. bPL Purification Column

[0354] The purpose of this column is to recover purified bPL for subsequent production of PPL (poly-propiolactone). Due to high boiling point of bPL (162°C at atmospheric pressure) this column is operated at pressures below atmospheric to limit the reboiler temperature below 105°C and avoid autopolymerization of bPL. The distillate stream from this column contains essentially pure bPL. The bottoms stream of this column contains residual bPL, SAH, residual carbonylation catalyst, and trace amounts of high boiling impurities. The Purified bPL stream is fed forward to Polymerization Reactor and bottoms stream is sent for disposal or recovery of residual bPL and SAH. The bottoms stream from THF recovery column containing bPL

(about 99.8wt%), SAH (about 0.1 wt%), residual carbonylation catalyst, and traces of low- and high-boiling impurities is fed to bPL Purification column.

[0355] The bPL purification column is in preferred form operated at the absolute pressure of about 60 Torrs (column is operated under vacuum) and the reboiler temperature is maintained at or below 105°C. The distillate stream consisting of essentially pure bPL (purity greater than 99.9wt%) with trace amounts of low- and high-boiling impurities is fed forward to bPL Polymerization reactor.

[0356] The Bottoms stream of this column consists of bPL (about 88.9wt%), SAH (about 9.7wt%), carbonylation catalyst (about 1.4wt%), and trace high-boiling impurities. The amount of bPL in this bottoms stream is selected to avoid crystallization of SAH at the temperatures below its melting point of 119°C and to limit the reboiler temperature to below 105°C.

Polypropiolactone Production system/production process

[0357] With reference to FIG. **2**, the relationship of the polypropiolactone production system/production process with other unit operations, such as the β-propiolactone purification system, the ion removal unit, and the glacial acrylic acid production system/production process, is depicted.

[0358] β-Propiolactone purification system **202** is configured to feed a β-propiolactone product stream into polypropiolactone production system/production process **210**. Homogeneous catalyst delivery system **204** is configured to feed a homogeneous polymerization catalyst into the polymerization reactor of polypropiolactone production system/production process **210**. Polypropiolactone production system/production process **210** is configured to polymerize β-propiolactone to produce polypropiolactone. Depending on the type of polymerization reactors selected and the configuration of such reactors, as well as the operating conditions (*e.g.*, operating temperature, operating pressure, and residence time) and

choice of polymerization catalysts used, the extent of conversion of the β-propiolactone may be controlled. In some variations, operating temperature is the average temperature of the contents of the reactor.

[0359] In some variations, partial conversion of β-propiolactone to polypropiolactone is achieved, and bPL recycle unit **220** is configured to recycle at least a portion of unreacted β-propiolactone to polypropiolactone production system/production process **210**. In other variations, complete conversion of β-propiolactone to polypropiolactone is achieved. The polypropiolactone product stream produced from polypropiolactone production system/production process **210** is fed glacial acrylic acid production system/production process **250**, which is configured to produce glacial acrylic acid from the polypropiolactone. Ion removal units **230** and **260** are present to remove at cationic and/or anionic carbonylation catalyst species that may be carried over from the upstream carbonylation reaction in the β-propiolactone production system/production process (not depicted in FIG. **2**). For example, when the carbonylation catalyst is a cobalt-aluminum compound, cobalt and aluminum species may be removed by ion removal units **230** and **260**. The ionic species isolated by the ion removal units may be disposed using unit **270**, or regenerated in unit **280** to produce an active carbonylation catalyst that may be recycled into the β-propiolactone production system/production process.

[0360] In some variations, unit **240** is configured to receive the polypropiolactone product stream (*e.g.*, in liquid form) from polypropiolactone production system/production process **210**, and is configured to pelletize, extrude, flake, or granulate the polypropiolactone product stream.

[0361] It should be understood, however, that FIG. **2** provides one exemplary configuration of these unit operations. In other variations, one or more of the unit operations depicted in FIG.

2 may be added, combined or omitted, and the order of the unit operations may be varied as well.

[0362] With reference again to FIG. 1, the polypropiolactone production system/production process is configured to produce polypropiolactone by polymerizing β-propiolactone in the presence of a polymerization catalyst. While FIG. **1** depicts the use of a single plug flow reactor for the polymerization of β-propiolactone to produce polypropiolactone, other reactor types and reactor configurations may be employed.

[0363] In some embodiments, the polypropiolactone production system/production process includes a β-propiolactone, a polymerization initiator or catalyst source, and at least one polymerization reactor.

BPL Source

[0364] With reference again to FIGS. **6-13**, the bPL entering the polypropiolactone production system/production process may be purified bPL from the bPL purification train or recycled bPL from the polymerization reactor, or a combination thereof.

[0365] In some embodiments, the inlet to the polymerization process can include at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3086 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 5000 kg/hr bPL, at least about 1000 kg/hr bPL, at least about 20000 kg/hr bPL, or at least about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 2000 kg/hr bPL, about 2500 kg/hr bPL, about 3000 kg/hr bPL, about 3500 kg/hr bPL, about 3638 kg/hr bPL, about 4000 kg/hr bPL, about 5000 kg/hr bPL, about 1000 kg/hr bPL, about 20000 kg/hr bPL, or about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include between about 2000 kg/hr bPL and about 3500 kg/hr bPL, between about 2500 kg/hr bPL and about 3500 kg/hr bPL, between about 3000 kg/hr bPL and about 3500 kg/hr bPL, between about 2000 kg/hr bPL

and about 35000 kg/hr bPL, between about 2500 kg/hr bPL and about 35000 kg/hr bPL, or between about 3000 kg/hr bPL and about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include at least about 25 kmol/hr bPL, at least about 30 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 42 kmol/hr bPL, or at least about 50 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.99, and at least about 0.993. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.99, and at least about 0.995. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, at most about 0.01, or at most about 0.004) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some variations, the remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm).

[0366] In some variations, the production stream entering the polymerization process further comprises other compounds, such as carbonylation catalyst or components thereof. For example, in some embodiments, the production stream further comprises cobalt or aluminum, or a combination thereof, from the carbonylation catalyst.

[0367] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen

compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0368] In certain variations, the production stream entering the polymerization process comprises cobalt. In some embodiments, the cobalt is Co^{-1}, Co, Co^{+}, Co^{2+}, or Co^{3+}, or a combination thereof. In some embodiments, the production stream has a cobalt concentration between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM and 0.015 mM.

[0369] In certain variations, the production stream entering the polymerization process comprises aluminum. In some embodiments, the concentration of aluminum in the production stream is between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM and 0.015 mM. In certain variations, the production stream entering the polymerization process contains less than 1ppm cobalt and less than 1ppm aluminum.

[0370] In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. The production stream entering the polymerization process can be the heavy (i.e., bottoms) stream from the BPL Purification system (e.g., BPL distillation system). In some embodiments, the production stream entering the polymerization process can have a temperature between about 30-120°C, between about 50-110°C, or about 70°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of at least about 0.05 bar, at least about 0.1 bar, at least about 5 bar, at least about 10 bar, at least about 15 bar, or at least about 20 bar. In some embodiments, production stream entering the polymerization process is between 0.05 bar and 20 bar, between 0.1 bar and 20 bar, between 5 bar and 15 bar, or between 10 bar and 20 bar.

[0371] In some variations, the mole ratio of bPL feed rate to the polymerization initiaor feed rate entering the polymerization process is from 500 to 20,000, from 1,000 to 10,000, from 2,000 to 9,000, from 3,000 to 8,000, from 5,000 to 7,000, from 1,000 to 110,000, from 5,000 to 110,000, from 25,000 to 110,000, from 50,000 to 110,000, or from 75,000 to 110,000. In one embodiment, mole ratio of bPL feed rate to the polymerization catalyst feed rate entering the polymerization process is from 1,000 to 9,000.

[0372] In some variations, bPL from the bPL purification process and bPL recycled from the polymerization process both enter the polymerization process. In certain embodiments, the weight ratio of recycled bPL to bPL from the bPL Purification process is from 0 to 0.01:0.99, from 0.4:0.6 to 0.1:0.9, from 0.5:0.5 to 0.15:0.85, from 0.35:0.65 to 0.1:0.9, or from 0.25:0.75 to 0.15:0.85.

Other Feed Sources

[0373] The polymerization process may further include other feed sources. For example, in one variation, the polymerization system further includes a polymerization initiator source, and the reactor is configured to receive a polymerization initiator from such source. In some variations, the polymerization initiator is a nucleophile.

Polymerization Conditions

[0374] In certain embodiments, conversion of bPL to PPL is performed in a continuous flow format. In certain embodiments, conversion of bPL to PPL is performed in a continuous flow format in the gas phase. In certain embodiments, conversion of bPL to PPL is performed in a continuous flow format in the liquid phase. In certain embodiments, conversion of bPL to PPL is performed in a liquid phase in a batch or semi-batch format. Conversion of bPL to PPL may be performed under a variety of conditions. In certain embodiments, the reaction may be performed in the presence of one or more catalysts that facilitate the transformation of the bPL to PPL.

[0375] In some embodiments, the production stream entering the polymerization process is a gas or a liquid. The conversion of bPL to PPL in the polymerization process may be performed in either the gas phase or the liquid phase and may be performed neat, or in the presence of a carrier gas, solvent, or other diluent.

[0376] In certain variations, the operating temperature of the polymerization reactor is maintained at or below the pyrolysis temperature of polypropiolactone. In some embodiments, the temperature of the reaction zone is maintained at or below about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 0 °C to about 200 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 25 °C to about 200 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 50 °C to about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 70 °C to about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 100 °C to about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 0 °C to about 100 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 50 °C to about 100 °C. In some variations, operating temperature is the average temperature of the contents of the reactor.

[0377] In some variations, the polymerization reactor is configured to produce PPL with a residence time from 1 second to 10 hours, from 1 second to 3 hours, from 1 min to 2 hours, from 1.5 min to 90 min, from 2 min to 75 min, from 2 min to 60 min, from 2 min to 45 min, from 3 min to 30 min, or from 4 min to 15 min. In one embodiment the residence time of the reaction mixture is from 2 min to 90 min. In certain variations, residence time refers to the length of time a material spends in a vessel (for example, a reaction vessel). It may be

calculated by specifying the volumetric flow rate of material and active volume of the vessel which the material is contained.

[0378] In some variations, the polymerization reactor is configured to produce PPL at an operating pressure from 0.01 bar to 100 bar, from 0.01 bar to 50 bar, from 0.1 bar to 30 bar, from 1 bar to 20 bar, from 2 bar to 15 bar, from 3 bar to 10 bar, from 0.01 bar to 15 bar, from 0.01 bar to 10 bar, from 0.1 bar to 5 bar, or from 0.1 bar to 2 bar. In some embodiments, the polymerization reactor is a CSTR and operating pressure in the reactor is from 0.1 bar to 5 bar. In other embodiments, the polymerization reactor is a PFR and the operating pressure in the reactor is from 1 bar to about 20 bar. In still other embodiments, the polymerization reactor is a loop reactor and the operating pressure in the reactor is from 1 bar to about 20 bar.

Homogeneous Catalysts and Initiators

[0379] Any suitable polymerization initiators and/or catalysts may be used to convert the BPL product stream entering the PPL production system/production process into a PPL product stream. In some embodiments, the polymerization initiator or catalyst is homogenous with the polymerization reaction mixture. Any suitable homogeneous polymerization initiator or catalyst capable of converting the production stream to the PPL product stream may be used in the methods described herein.

[0380] Catalysts suitable for the ring-opening polymerization step of the methods disclosed herein are disclosed, for example, in: Journal of the American Chemical Society (2002), 124(51), 15239-15248 Macromolecules, vol. 24, No. 20, pp. 5732-5733, Journal of Polymer Science, Part A-1, vol. 9, No. 10, pp. 2775-2787; Inoue, S., Y. Tomoi, T. Tsuruta & J. Furukawa; Macromolecules, vol. 26, No. 20, pp. 5533-5534; Macromolecules, vol. 23, No. 13, pp. 3206-3212; Polymer Preprints (1999), 40(1), 508-509; Macromolecules, vol. 21, No. 9, pp. 2657-2668; and Journal of Organometallic Chemistry, vol. 341, No. 1-3, pp. 83-9; and in US

Patent Nos. 3,678,069, 3,169,945, 6,133,402; 5,648,452; 6,316,590; 6,538,101; and 6,608,170. The entirety of each of which is hereby incorporated herein by reference.

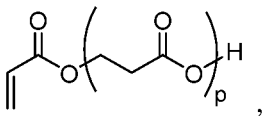
[0381] The polymerization process may further comprise a polymerization initiator including but not limited to amines, polyamines, phosphines amongst others. Further, a variety of polymerization initiators may be used in the polymerization process, including by not limited to -carbonates of alkali- and alkaline earth metals.

[0382] In certain embodiments, suitable polymerization – initiators include carboxylate salts of metal ions or organic cations.

[0383] In certain embodiments, a polymerization initiator is combined with the production stream containing bPL. In certain embodiments, the molar ratio of the polymerization initiator to the bPL in the production stream is about 1:15000. In certain embodiments, the molar ratio of polymerization intiator:bPL is about 1:100, 1:10000, 1:1000, 1:20000 or a range including any two of these ratios.

[0384] In certain embodiments, where the polymerization ~~catalyst~~ initiator comprises a carboxylate salt, the carboxylate has a structure such that upon initiating polymerization of bPL, the polymer chains produced have an acrylate chain end. In certain embodiments, the carboxylate ion on a polymerization initiator is the anionic form of a chain transfer agent used in the polymerization process.

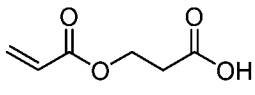
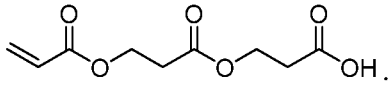
[0385] In certain embodiments, the carboxylate salt of the polymerization initiator is a salt of (i.e., the anionic form) a compound of Formula (**A**):



,

(**A**)

or a mixture of any two or more of these, where *p* is from 0 to 9. In certain embodiments, *p* is from 0 to 5. In certain embodiments, the carboxylate salt of the polymerization ~~catalyst~~ initiator is an acrylate salt (i.e. compound of Formula (**A**) where p = 0).

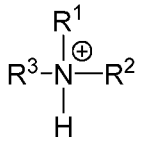
[0386] In certain embodiments, the carboxylate salt of the polymerization initiator is a salt of an acrylic acid dimer, . In certain embodiments, the carboxylate salt of the polymerization ~~catalyst~~ initiator is a salt of an acrylic acid trimer, .

[0387] In certain embodiments, where the polymerization initiator comprises a carboxylate salt, the carboxylate is the anionic form of a C_{1-40} carboxylic acid. In certain embodiments, the carboxylate salt can be a salt of a polycarboxylic acid (e.g. a compound having two or more carboxylic acid groups). In certain embodiments, the carboxylate comprises the anion of a C_{1-20} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of a C_{1-12} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of a C_{1-8} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of a C_{1-4} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of an optionally substituted benzoic acid. In certain embodiments, the carboxylate is selected from the group consisting of: formate, acetate, propionate, valerate, butyrate, C_{5-10} aliphatic carboxylate, and C_{10-20} aliphatic carboxylate.

[0388] As noted, in certain embodiments, the polymerization initiator comprises a carboxylate salt of an organic cation. In certain embodiments, the polymerization initiator comprises a carboxylate salt of a cation wherein the positive charge is located at least partially on a nitrogen, sulfur, or phosphorus atom. In certain embodiments, the polymerization initiator comprises a carboxylate salt of a nitrogen cation. In certain embodiments, the polymerization initiator comprises a carboxylate salt of a cation selected from the group consisting of:

ammonium, amidinium, guanidinium, a cationic form of a nitrogen heterocycle, and any combination of two or more of these. In certain embodiments, the polymerization ~~catalyst~~ initiator comprises a carboxylate salt of a phosphorus cation. In certain embodiments, the polymerization ~~catalyst~~ initiator comprises a carboxylate salt of a cation selected from the group consisting of: phosphonium and phosphazenium. In certain embodiments, the polymerization ~~catalyst~~ initiator comprises a carboxylate salt of a sulfur-containing cation. In certain embodiments, the polymerization initiator comprises a sulfonium salt.

[0389] In certain embodiments, the polymerization initiator comprises a carboxylate salt of a protonated amine:



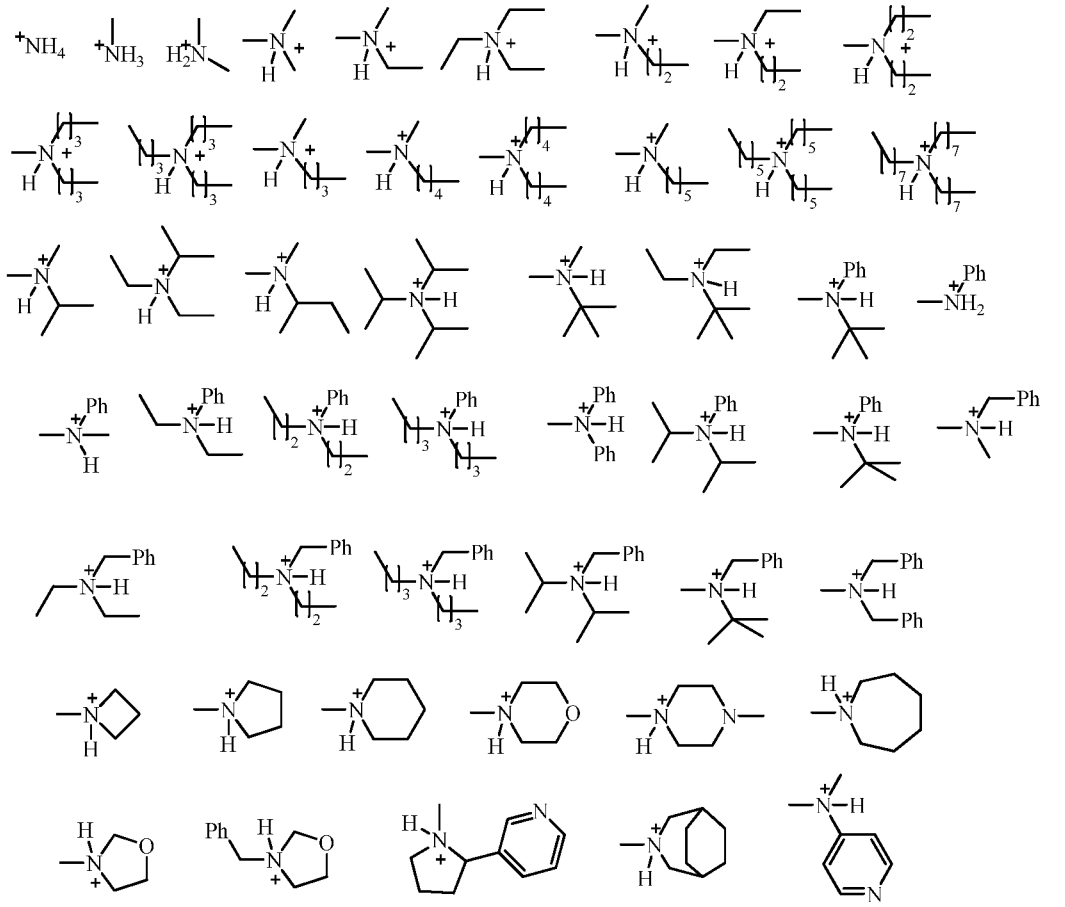
,

wherein:

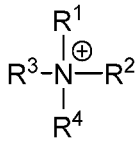
each R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7- to 14-membered saturated or partially unsaturated polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an 8- to 14-membered polycyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated monocyclic heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 14-membered saturated or partially unsaturated polycyclic heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; phenyl; or an 8- to 14-membered polycyclic aryl ring; wherein R^1 and R^2 can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; each R^3 is independently hydrogen or an optionally substituted radical

selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7- to 14-membered saturated or partially unsaturated polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an 8- to 14-membered polycyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated monocyclic heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 14-membered saturated or partially unsaturated polycyclic heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; phenyl; or an 8- to 14-membered polycyclic aryl ring; wherein an R^3 group can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

[0390] In certain embodiments where the polymerization initiator comprises a carboxylate salt of a protonated amine, the protonated amine is selected from the group consisting of:



[0391] In certain embodiments, the polymerization initiator comprises a carboxylate salt of a quaternary ammonium salt:

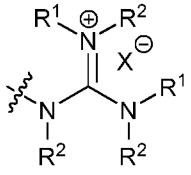


wherein:

each R^1, R^2 and R^3 is described above; and

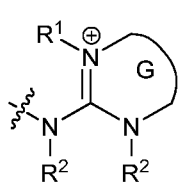
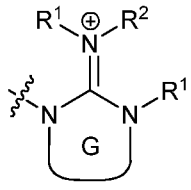
each R^4 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7- to 14-membered saturated or partially

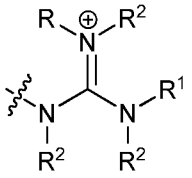
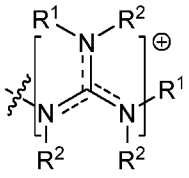
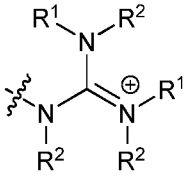
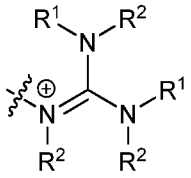
unsaturated polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an 8- to 14-membered polycyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated monocyclic heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 14-membered saturated or partially unsaturated polycyclic heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; phenyl; or an 8- to 14-membered polycyclic aryl ring; wherein an R^4 group can be taken with an R^1, R^2 or R^3 group to form one or more optionally substituted rings.

[0392] In certain embodiments, the polymerization initiator comprises a carboxylate salt of a guanidinium group:  , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein. In certain embodiments, each R^1 and R^2 is independently hydrogen or C_{1-20} aliphatic. In certain embodiments, each R^1 and R^2 is independently hydrogen or C_{1-12} aliphatic. In certain embodiments, each R^1 and R^2 is independently hydrogen or C_{1-20} heteroaliphatic. In certain embodiments, each R^1 and R^2 is independently hydrogen or phenyl. In certain embodiments, each R^1 and R^2 is independently hydrogen or 8- to 10-membered aryl. In certain embodiments, each R^1 and R^2 is independently hydrogen or 5- to 10-membered heteroaryl. In certain embodiments, each R^1 and R^2 is independently hydrogen or 3- to 7-membered heterocyclic. In certain embodiments, one or more of R^1 and R^2 is optionally substituted C_{1-12} aliphatic.

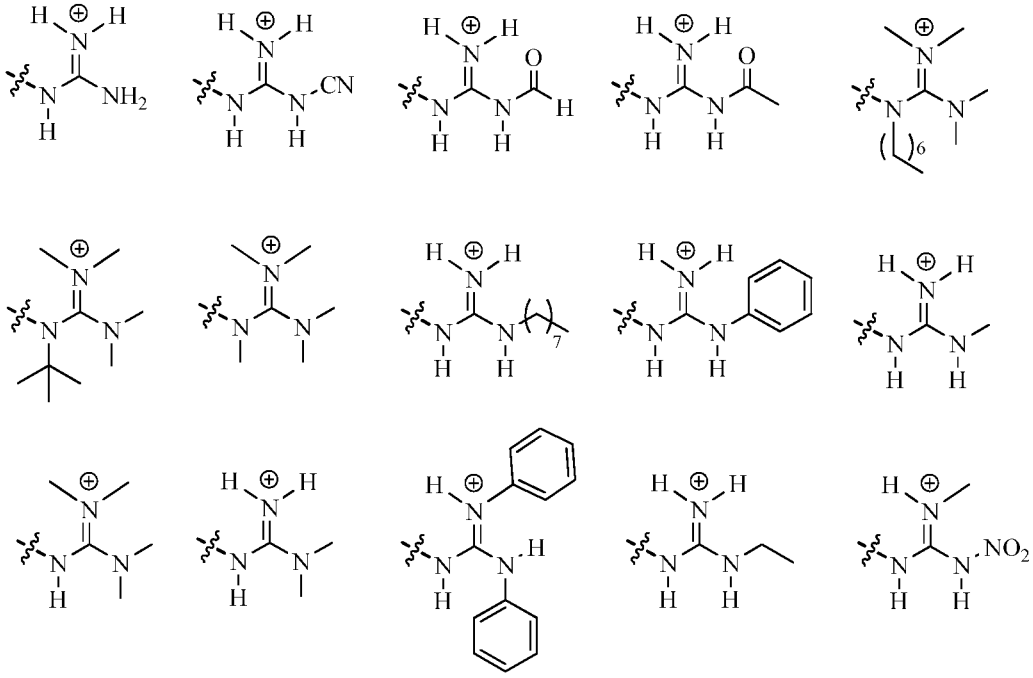
[0393] In certain embodiments, any two or more R^1 or R^2 groups are taken together with intervening atoms to form one or more optionally substituted carbocyclic, heterocyclic, aryl, or heteroaryl rings. In certain embodiments, R^1 and R^2 groups are taken together to form an

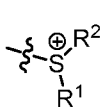
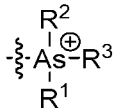
optionally substituted 5- or 6-membered ring. In certain embodiments, three or more R^1 and/or R^2 groups are taken together to form an optionally substituted fused ring system.

[0394] In certain embodiments, an R^1 and R^2 group are taken together with intervening atoms to form a compound selected from:  or , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein, and Ring G is an optionally substituted 5- to 7-membered saturated or partially unsaturated heterocyclic ring.

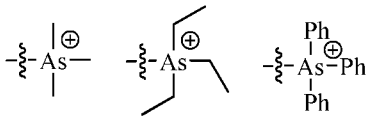
[0395] It will be appreciated that when a guanidinium cation is depicted as , all such resonance forms are contemplated and encompassed by the present disclosure. For example, such groups can also be depicted as , , or .

[0396] In specific embodiments, a guanidinium cation is selected from the group consisting of:

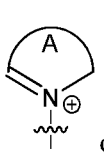
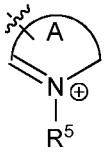


[0397] In certain embodiments, a polymerization - initiator comprises a carboxylate salt of a sulfonium group or an arsonium group:  or , wherein each of R^1, R^2, and R^3 are as defined above and described in classes and subclasses herein.

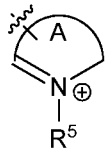
[0398] In specific embodiments, an arsonium cation is selected from the group consisting of:

.

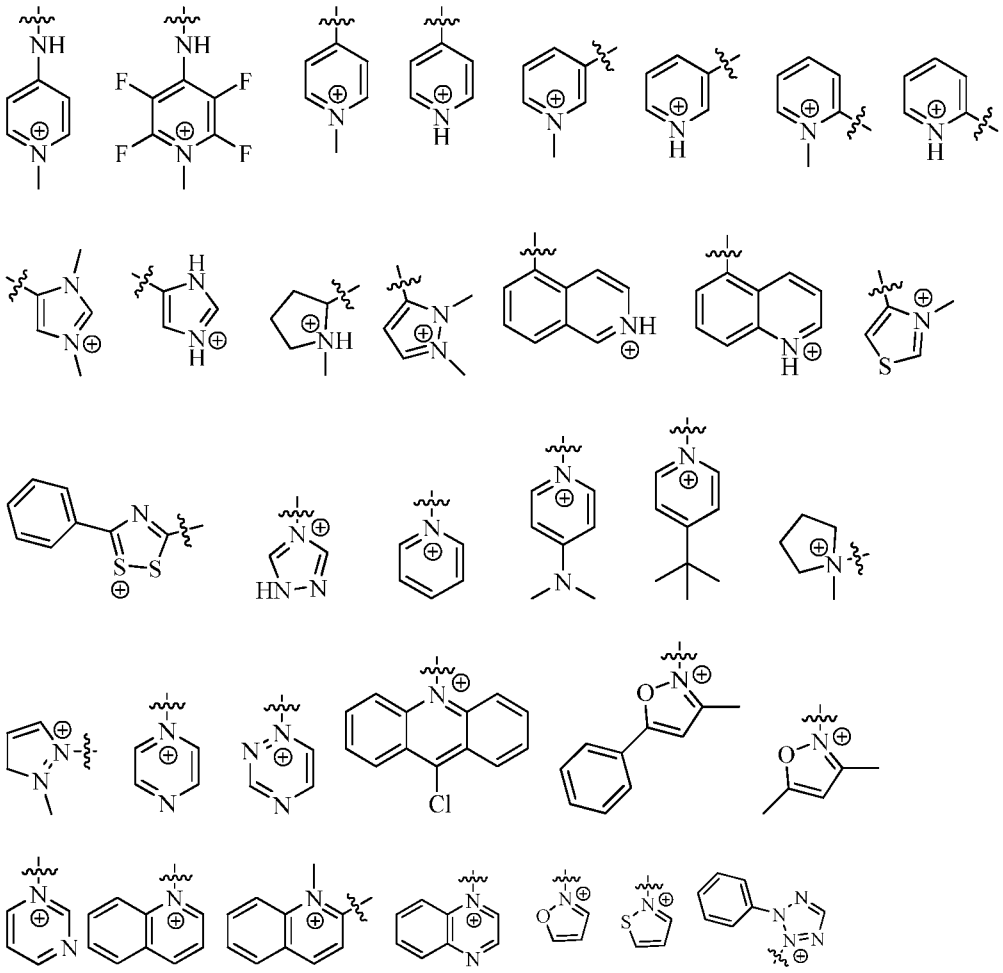
[0399] In certain embodiments, a polymerization initiator comprises a carboxylate salt of an optionally substituted nitrogen-containing heterocycle. In certain embodiments, the nitrogen-containing heterocycle is an aromatic heterocycle. In certain embodiments, the optionally substituted nitrogen-containing heterocycle is selected from the group consisting of: pyridine, imidazole, pyrrolidine, pyrazole, quinoline, thiazole, dithiazole, oxazole, triazole, pyrazolem, isoxazole, isothiazole, tetrazole, pyrazine, thiazine, and triazine.

[0400] In certain embodiments, a nitrogen-containing heterocycle includes a quaternarized nitrogen atom. In certain embodiments, a nitrogen-containing heterocycle includes an iminium moiety such as  or . In certain embodiments, the optionally substituted nitrogen-containing heterocycle is selected from the group consisting of pyridinium, imidazolium, pyrrolidinium, pyrazolium, quinolinium, thiazolium, dithiazolium, oxazolium, triazolium, isoxazolium, isothiazolium, tetrazolium, pyrazinium, thiazinium, and triazinium.

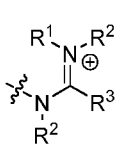
[0401] In certain embodiments, a nitrogen-containing heterocycle is linked to a metal complex via a ring nitrogen atom. In certain embodiments, a ring nitrogen to which the attachment is made is thereby quaternized, and In certain embodiments, linkage to a metal complex takes the place of an N-H bond and the nitrogen atom thereby remains neutral. In certain embodiments, an optionally substituted *N*-linked nitrogen-containing heterocycle is a pyridinium derivative. In certain embodiments, optionally substituted *N*-linked nitrogen-containing heterocycle is an imidazolium derivative. In certain embodiments, optionally substituted N-linked nitrogen-containing heterocycle is a thiazolium derivative. In certain embodiments, optionally substituted N-linked nitrogen-containing heterocycle is a pyridinium derivative.

[0402] In certain embodiments, a polymerization initiator comprises a carboxylate salt of . In certain embodiments, ring A is an optionally substituted, 5- to 10-membered heteroaryl group. In certain embodiments, Ring A is an optionally substituted, 6-membered heteroaryl group. In certain embodiments, Ring A is a ring of a fused heterocycle. In certain embodiments, Ring A is an optionally substituted pyridyl group.

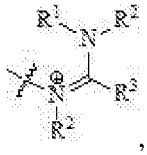
[0403] In specific embodiments, a nitrogen-containing heterocyclic cation is selected from the group consisting of:



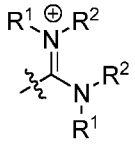
[0404] In certain embodiments, a polymerization initiator comprises a carboxylate salt of

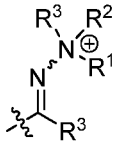


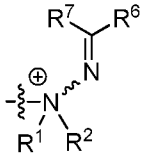
or



, where each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

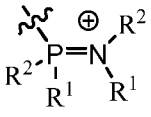
[0405] In certain embodiments, a polymerization initiator comprises a carboxylate salt of , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

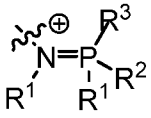
[0406] In certain embodiments, a polymerization initiator comprises a carboxylate salt of  wherein each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

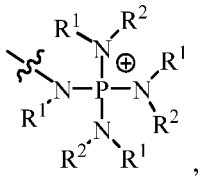
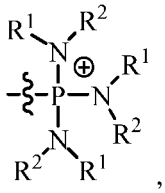
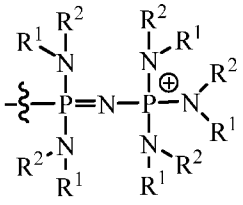
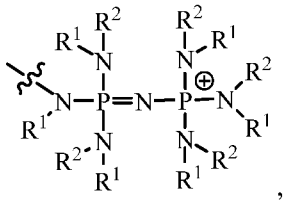
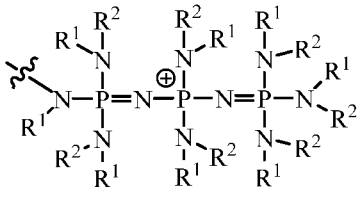
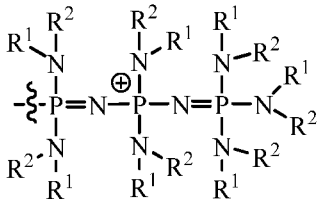
[0407] In certain embodiments, a polymerization initiator comprises a carboxylate salt of , wherein each of R^1, R^2, R^6, and R^7 is as defined above and described in classes and subclasses herein.

[0408] In certain embodiments, R^6 and R^7 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl, and 8-10-membered aryl. In certain embodiments, R^6 and R^7 are each independently an optionally substituted C_{1-20} aliphatic. In certain embodiments, R^6 and R^7 are each independently an optionally substituted C_{1-20} heteroaliphatic having. In certain embodiments, R^6 and R^7 are each independently an optionally substituted phenyl or 8-10-membered aryl. In certain embodiments, R^6 and R^7 are each independently an optionally substituted 5- to10-membered heteroaryl. In certain embodiments, R^6 and R^7 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3-C_{14} carbocycle, optionally substituted C_3-C_{14} heterocycle, optionally substituted C_6-C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In certain embodiments, R^6 and R^7 are

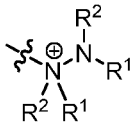
each independently an optionally substituted C_{1-6} aliphatic. In certain embodiments, each occurrence of R^6 and R^7 is independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In certain embodiments, each occurrence of R^6 and R^7 is independently perfluoro. In certain embodiments, each occurrence of R^6 and R^7 is independently $-CF_2CF_3$.

[0409] In certain embodiments, a polymerization initiator comprises a carboxylate salt of  wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

[0410] In certain embodiments, a polymerization initiator comprises a carboxylate salt of  wherein each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

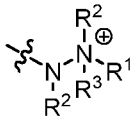
[0411] In certain embodiments, a cation is , , , , , or , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

[0412] In certain embodiments, a polymerization initiator comprises a carboxylate salt of



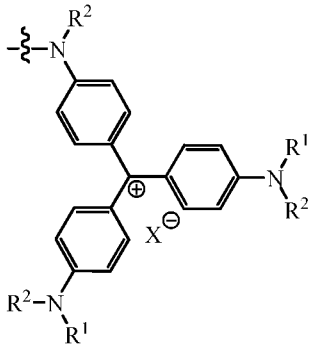
wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

[0413] In certain embodiments, a polymerization initiator comprises a carboxylate salt of



wherein each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

[0414] In certain embodiments, a polymerization initiator comprises a carboxylate salt of



, wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein. In certain embodiments, suitable initiator include transition metal compounds. In certain embodiments, suitable catalysts include acid catalysts. In certain embodiments, the catalyst is a heterogeneous catalyst.

[0415] In some embodiments, the homogeneous polymerization initiator is a quaternary ammonium salt (for example, tetrabutylammonium (TBA) acrylate, TBA acetate, trimethylphenylammonium acrylate, or trimethylphenylammonium acetate) or a phosphine (for example, tetraphenyl phosphonium acrylate).

[0416] In some embodiments, the catalyst is tetrabutylammonium acrylate, sodium acrylate, potassium acrylate, iron chloride, tetrabutylammonium acetate,

trimethylphenylammonium acrylate, trimethylphenylammonium acetate, or tetraphenyl phosphonium acrylate.

[0417] With reference to FIG. **4A**, the polymerization catalyst in the first reactor (**408**) and the additional polymerization initiator in the second reactor (**410**) may be the same or different. For example, in some embodiments, wherein the same initiator is used in both reactors, concentration of initiator is not the same in each reactor.

[0418] In some embodiments, the homogeneous polymerization initiator is added to a polymerization reactor as a liquid. In other embodiments it is added as a solid, which then becomes homogeneous in the polymerization reaction. In some embodiments where the polymerization initiator is added as a liquid, the polymerization initiator may be added to the polymerization reactor as a melt or in any suitable solvent. For example, in some variations GAA, molten PPL or bPL is used as a solvent.

[0419] In some embodiments, the solvent for the polymerization initiator is selected such that the initiator is soluble, the solvent does not contaminate the product polymer, and the solvent is dry. In some variations, the polymerization initiator solvent is GAA, molten PPL, or bPL. In certain variations, solid PPL is added to a polymerization reactor, heated above room temperature until liquid, and used as the polymerization initiator solvent. In other embodiments, bPL is added to the polymerization reactor, cooled below room temperature until liquid, and used as the polymerization initiator solvent.

[0420] In some variations, the solid or liquid polymerization initiator (as a melt or as a solution in a suitable solvent) is prepared in one location, then shipped to a second location where it is used in the polymerization reactor. In other embodiments, the solid or liquid polymerization initiator (as a melt or as a solution in a suitable solvent) is prepared at the location of the polymerization reactor (for example, to reduce exposure to moisture and/or oxygen).

[0421] A solid or liquid polymerization initiator (as a melt or as a solution in a suitable solvent) may be pumped into a stirred holding tank or directly into the polymerization reactor.

[0422] In some variations, the liquid initiator and/or initiator precursors are dispensed from a shipping vessel/container into an intermediate, inert vessel to be mixed with suitable solvent, and then the initiator solution is fed to the reactor or a pre-mix tank. The initiator preparation system and the connections may be selected in such a way to ensure that the initiator or precursors are not contacted by ambient atmosphere.

[0423] In some variations, the polymerization reactor is a PFR, the solid or liquid initiator (as a melt or as a solution in a suitable solvent) and bPL are fed to a small stirred tank and then the mixture is fed to the PFR. In other embodiments, the bPL and the liquid catalyst are fed to a pre-mixer installed at the inlet of the PFR. In yet another embodiment, the PFR has a static mixer, the reaction occurs on the shell side of the reactor, and the solid or liquid initiator and bPL are introduced at the inlet of the reactor and the static mixer elements mix the initiator and bPL. In still another embodiments, the PFR has a static mixer, the reaction occurs on the shell side of the reactor, and the solid or liquid initiator is introduced into the PFR using metering pumps/feeders at multiple locations distributed along the lengths of the reactor.

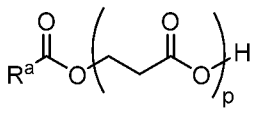
[0424] In some embodiments, the homogeneous polymerization initiator is delivered to the location of the polymerization reactor as a solid (for example, solid Al(TPP)Et, solid sodium acrylate, solid potassium acrylate, solid sodium acetate, solid potassium acetate, or solid TBA acrylate), the solid initiator is unpacked and loaded in hoppers under inert conditions (CO or inert gas), and the solids from hoppers can be fed directly inot the polymerization reactor, or be mixed with bPL prior to the reactor, or be metered into a suitable solvent before pumping into the polymerization reactors or mixing tanks.

Heterogeneous System

[0425] Any suitable polymerization catalyst may be used in the polymerization process to convert the production stream entering the polymerization process to the PPL product stream. In some embodiments, the polymerization catalyst is heterogeneous with the polymerization reaction mixture. Any suitable heterogeneous polymerization catalyst capable of polymerizing bPL in the production stream to produce the PPL product stream may be used in the methods described herein.

[0426] In some embodiments, the heterogeneous polymerization catalyst comprises any of the homogeneous polymerization catalysts described above, supported on a heterogeneous support. Suitable heterogeneous supports may include, for example, amorphous supports, layered supports, or microporous supports, or any combination thereof. Suitable amorphous supports may include, for example, metal oxides (such as aluminas or silicas) or carbon, or any combination thereof. Suitable layered supports may include, for example, clays. Suitable microporous supports may include, for example, zeolites (such as molecular sieves) or cross-linked functionalized polymers. Other suitable supports may include, for example, glass surfaces, silica surfaces, plastic surfaces, metal surfaces including zeolites, surfaces containing a metallic or chemical coating, membranes (comprising, for example, nylon, polysulfone, silica), micro-beads (comprising, for example, latex, polystyrene, or other polymer), and porous polymer matrices (comprising, for example, polyacrylamide, polysaccharide, polymethacrylate).

[0427] In some variations, the heterogeneous polymerization catalyst comprises the carboxylate salt of any of the homogeneous polymerization catalysts described above, wherein the carboxylate is heterogeneous. For example, in certain embodiments, the carboxylate of the polymerization catalyst is a compound of Formula (**D**):


(**D**),

where *p* is from 0 to 9 and R^a is a non-volatile moiety. The term "non-volatile moiety," as used herein, refers to a moiety or material to which a carboxylate can be attached, and that renders the carboxylate (e.g., when p = 0) non-volatile to pyrolysis conditions. In some embodiments, a non-volatile moiety is selected from the group consisting of glass surfaces, silica surfaces, plastic surfaces, metal surfaces including zeolites, surfaces containing a metallic or chemical coating, membranes (comprising, for example, nylon, polysulfone, silica), micro-beads (comprising, for example, latex, polystyrene, or other polymer), and porous polymer matrices (comprising, for example, polyacrylamide, polysaccharide, polymethacrylate). In some embodiments, the non-volatile moiety has a molecular weight above 100, 200, 500, or 1000 g/mol. In some embodiments, the non-volatile moiety is part of a fixed or packed bed system. In some embodiments, the non-volatile moiety is part of a fixed or packed bed system comprising pellets (e.g., zeolite). In certain embodiments, *p* is from 0 to 5. In certain embodiments, the carboxylate salt of the polymerization catalyst is an acrylate salt (i.e., of compound of Formula (**D**) where p = 0).

[0428] In some embodiments, the heterogeneous polymerization catalyst is a solid-supported quaternary ammonium salt (for example, tetrabutylammonium (TBA) acrylate, TBA acetate, trimethylphenylammonium acrylate, or trimethylphenylammonium acetate) or a phosphine (for example, tetraphenyl phosphonium acrylate).

[0429] In some embodiments, the catalyst is solid-supported tetrabutylammonium acrylate, iron chloride, TBA acetate, trimethylphenylammonium acrylate, trimethylphenylammonium acetate, or tetraphenyl phosphonium acrylate.

[0430] In certain embodiments, conversion of the production stream entering the polymerization process to the PPL product stream utilizes a solid carboxylate catalyst and the conversion is conducted at least partially in the gas phase. In certain embodiments, the solid carboxylate catalyst in the polymerization process comprises a solid acrylic acid catalyst. In

certain embodiments, the production stream enters the polymerization process as a liquid and contacted with a solid carboxylate catalyst to form the PPL product stream. In other embodiments, the production stream enters the polymerization process as a gas and contacted with a solid carboxylate catalyst to form the PPL product stream.

[0431] In some variations, the polymerization catalyst is a heterogeneous catalyst bed. Any suitable resin may be used for such a heterogeneous catalyst bed. In one embodiment, the polymerization catalyst is a heterogeneous catalyst bed packed in a tubular reactor. In some embodiments, the polymerization reactor system comprises a plurality of heterogeneous catalyst beds, wherein at least one catalyst bed is being used in the polymerization reactor, and at least one catalyst bed is not being used in the polymerization reactor at the same time. For example, the catalyst bed not actively being used may be being regenerated for later use, or may be stored as a back-up catalyst bed in case of catalyst failure of the actively used bed. In one embodiment, the polymerization reactor system comprises three heterogeneous catalyst beds, wherein one catalyst bed is being used in the polymerization reactor, one catalyst bed is being regenerated, and one catalyst bed is being stored as a back-up in case of catalyst failure.

[0432] In some variations, the heterogeneous polymerization catalyst is prepared in one location, then shipped to a second location where it is used in the polymerization reactor. In other embodiments, the heterogeneous polymerization catalyst is prepared at the location of the polymerization reactor (for example, to reduce exposure to moisture and/or oxygen).

Solvents

[0433] In some embodiments, the polymerization process does not include solvent. In other embodiments, the polymerization process does include one or more solvents. Suitable solvents can include, but are not limited to: hydrocarbons, ethers, esters, ketones, nitriles, amides, sulfones, halogenated hydrocarbons, and the like. In certain embodiments, the solvent is selected such that the PPL product stream is soluble in the reaction medium.

[0434] Without wishing to be bound by any particular theory, it is believed that solvents comprising Lewis bases of low to moderate polarity improve the performance of the polymerization reaction. Thus, in certain embodiments, a polymerization solvent comprises a Lewis base and is less polar than 1,3-dioxane (ε = dielectric constant at 20 °C = 13.6). In certain embodiments, a polymerization solvent comprises a Lewis base and is less polar than ortho-difluorobenzene (ε = 13). In certain embodiments, a polymerization solvent comprises a Lewis base and is less polar than metadifluorobenzene (ε = 5). In certain embodiments, a polymerization solvent comprises a Lewis base with substantially the same polarity as 1 ,4-dioxane (ε = 2.2). In some embodiments, a polymerization solvent is less polar than a carbonylation solvent as measured by dielectric constant. In some embodiments, a polymerization solvent has a dielectric constant at 20°C of less than about 13.6, less than about 13, or less than about 5.

[0435] For example, with reference to polymerization process depicted in FIGS. **4A** and **4B**, reactors **408** and/or **410** may be configured to receive solvent. For example, in one variation, polymerization process may further include a solvent source configured to feed solvent into reactors **408** and **410**. In another variation, the bPL from production stream **402** may be combined with solvent to form the production stream containing bPL fed into reactor **408**. In yet another variation, the polymerization catalyst from polymerization catalyst sources **404** and/or **406** may be combined with a solvent to form polymerization catalyst streams fed into the reactors.

Polymerization Reactors

[0436] The one or more polymerization reactors in the polymerization process may be any suitable polymerization reactors for the production of the PPL product stream from the production stream entering the polymerization process. For example, the polymerization reactor may be a CSTR, loop reactor, or plug flow reactor, or a combination thereof. In some

embodiments, the polymerization process comprises a single reactor, while in other embodiments, the polymerization process comprises a plurality of reactors. In some variations, the bPL is completely converted to PPL in a polymerization reactor. In other variations, the bPL is not completely converted to PPL in a polymerization reactor, and the PPL stream exiting the polymerization reactor comprises unreacted bPL. In certain variations, the PPL stream comprising unreacted bPL is directed to a bPL/PPL separator to remove the bPL from the PPL. The bPL may then be recycled back into the polymerization reactor, as described, for example, in FIGS. **7**, **9**, **11** and **13** above.

[0437] In certain variations, the polymerization process comprises two reactors in series, wherein the purified bPL stream enters the first reactor and undergoes incomplete polymerization to produce a first polymerization stream comprising PPL and unreacted bPL, the first polymerization stream exits the outlet of the first reactor and enters the inlet of the second reactor to undergo additional polymerization. In some variations, the additional polymerization completely converts the bPL to PPL, and the PPL product stream exits the outlet of the second polymerization reactor.

[0438] In other variations, the additional polymerization incompletely converts the bPL to PPL, and the PPL product stream exiting the outlet of the second polymerization reactor comprises PPL and unreacted bPL. In certain variations, the PPL product stream enters a BPL /PPL separator to remove unreacted bPL from the PPL product stream. In certain variations, the unreacted bPL is recycled back into the polymerization process. For example, in some variations, the unreacted bPL is recycled to the first polymerization reactor or the second polymerization reactor, or both the first and the second polymerization reactors.

[0439] In some embodiments, the polymerization process comprises a series of one or more continuous CSTR reactors followed by a BPL/PPL separator (such as a wiped film evaporator (WFE) or flash tank evaporator operating under vacuum). In other embodiments, the

polymerization process comprises a series of one or more loop reactors followed by a BPL/PPL separator (such as a WFE or flash tank evaporator operating under vacuum). In yet other embodiments, the polymerization process comprises a series of one or more in a series of one or more CSTR reactors followed by a polishing plug flow reactor (PFR) or by a BPL/PPL separator (Wiped Film Evaporator or flash tank evaporator operating under vacuum). In still other embodiments, the polymerization process comprises a series of one or more PFR optionally followed by a BPL/PPL separator (such as a WFE or flash tank evaporator operating under vacuum).

[0440] In some embodiments, the polymerization process comprises greater than two polymerization reactors. For example, in certain embodiments, the polymerization process comprises three or more polymerization reactors, four or more polymerization reactors, five or more polymerization reactors, six or more polymerization reactors, seven or more polymerization reactors, or eight or more polymerization reactors. In some variations, the reactors are arranged in series, while in other variations, the reactors are arranged in parallel. In certain variations, some of the reactors are arranged in series while others are arranged in parallel.

[0441] FIGS. **4A** and **4B** depict exemplary PPL production system/production processs comprising two polymerization reactors connected in series, and a PPL purification and BPL recycle system with a wiped film evaporator (WFE) for recycling of unreacted bPL back into the polymerization reactors. With reference to FIG. **4A**, the polymerization process includes bPL source **402** and polymerization catalyst source **404**, configured to feed bPL and catalyst, respectively, into reactor **408**. Reactor **408** includes a bPL inlet to receive bPL from the bPL source and a polymerization catalyst inlet to receive polymerization catalyst from the polymerization catalyst source. In some variations, the bPL inlet is configured to receive the bPL from the bPL source at a rate of 3100 kg/hr, and the first polymerization catalyst inlet is

configured to receive the polymerization catalyst from the polymerization catalyst source at a rate of 0.1 to 5 kg/hr.

[0442] With reference again to FIG. **4A**, reactor **408** further includes a mixture outlet to output a mixture comprising PPL, unreacted bPL, and residual carbonylation catalyst to reactor **410**. Reactor **410** is a second reactor positioned after reactor **408**, and is configured to receive the mixture from reactor **408** and additional polymerization catalyst from polymerization catalyst source **406**. In some variation, the mixture inlet of the second reactor is configured to receive the mixture from the first reactor at a rate of 4500 kg/hr, and the second polymerization catalyst inlet is configured to receive additional polymerization catalyst from the catalyst source at a rate of 0.1 to 4 kg/hr.

[0443] With reference again to FIG. **4A**, reactor **408** further includes a mixture outlet to output a mixture comprising PPL, unreacted bPL, and residual carbonylation catalyst to evaporator **412**. In some variations, the mixture outlet is configured to output such mixture at a rate of 4500 kg/hr.

[0444] With reference to FIG. **4B**, the depicted polymerization process includes bPL source **422** and polymerization catalyst source **424**, configured to feed bPL and catalyst, respectively, into reactor **428**. Reactor **428** includes a bPL inlet to receive bPL from the bPL source and a polymerization catalyst inlet to receive polymerization catalyst from the polymerization catalyst source. In some variations, the bPL inlet is configured to receive the bPL from the bPL source at a rate of 3100 kg/hr, and the first catalyst inlet is configured to receive the catalyst from the catalyst source at a rate of 0.1 to 5 kg/hr.

[0445] With reference again to FIG. **4B**, reactor **428** further includes a mixture outlet to output a mixture comprising PPL, unreacted bPL, and residual carbonylation catalyst to reactor **430**. Reactor **430** is a second reactor positioned after reactor **428**, and is configured to receive the mixture from reactor **428** and additional polymerization catalyst from polymerization

catalyst source **426**. In some variation, the mixture inlet of the second reactor is configured to receive the mixture from the first reactor at a rate of 4500 kg/hr, and the second polymerization catalyst inlet is configured to receive additional polymerization catalyst from the polymerization catalyst source at a rate of 0.1 to 4 kg/hr.

[0446] In some variations, the mixture output from reactor **410** (FIG. **4A**) and reactor **430** (FIG. **4B**) is made up of at least 95 %wt PPL.

[0447] Such mixture may be output from the second reactor to an evaporator. Evaporator **412** (FIG. **4A**) and **432** (FIG. **4B**) may be, for example, a wiped film evaporator, thin film evaporator, or falling film evaporator. The evaporator is configured to produce a PPL product stream.

[0448] In some variations, the evaporator is configured to produce a PPL product stream having a purity of at least 98%, at least 98.5%, or at least 99%. In other variations, the evaporator is configured to produce a PPL product stream having less 0.6 % wt of bPL. In some variations, the PPL stream has trace amounts of carbonylation catalyst. For example, the PPL product stream may have 0.1 mM of cobalt from the carbonylation catalyst. In some variations, the trace amounts of carbonylation catalyst are subsequently removed from the PPL product stream by IER before thermolysis, as described above in FIGS. **6**, **7**, **10** and **11**.

[0449] In some variations, the polymerization process further includes one or more heat exchangers. With reference to FIG. **4A**, bPL from bPL source **402** may be passed through heat exchanger **414** before such BPL stream is fed into reactor **408**.

[0450] It should generally be understood that the polymerization is an exothermic reaction. Thus, in other variations, reactors **408** and **410** (FIG. **4A**) may further include a connection to at least one heat exchanger. With reference to FIG. **4B**, reactors **428** and **430** (FIG. **4B**) may further include a connection to at least one heat exchanger.

[0451] The reactors of polymerization process may include any suitable reactors, including, for example, continuous reactors or semi-batch reactors. In one variation, with reference to FIG. **4A**, the reactors may be continuous-flow stirred-tank reactors. The reactors may also include the same or different stirring devices. For example, in one variation, reactor **408** may include a low velocity impeller, such as a flat blade. In other variation, reactor **410** may include a low shear mixer, such as a curved blade.

[0452] A skilled artisan would recognize that the choice for the mixing device in each of the reactors may depend on various factors, including the viscosity of the mixture in the reactor. For example, the mixture in the first reactor may have a viscosity less than 1000 cP. If the viscosity is less than1000 cP, then a low velocity impeller may be desired. In another example, the mixture in the second reactor may have a viscosity greater than 2000 cP. If the viscosity is greater than 2000 cP, then a low shear mixer may be desired.

[0453] In another variation, with reference to FIG. **4B**, the reactors may be loop reactors.

[0454] It should be understood that while FIGS. **4A** and **4B** depict the use of two reactors configured in series, other configurations are considered. For example, in other exemplary variations of the polymerization process, three reactors may be employed. In yet other variations where a plurality of reactors is used in the polymerization process, they may be arranged in series or in parallel.

[0455] FIG. **5** depicts yet another exemplary polymerization process, which includes a BPL polymerization reactor. Polymerization reactor **500** includes mixing zone **510** configured to mix the production stream entering the polymerization process and catalyst, and a plurality of cooling zones **520** positioned after the mixing zone. Polymerization reactor **500** has reaction length **502**, wherein up to 95% of the bPL in the entering production stream is polymerized in the presence of the catalyst to form PPL in the first 25% of the reaction length. In some variations of the system depicted in FIG. **5**, the bPL is completely converted to PPL. Such a

system may be used, for example, in the complete conversion of bPL to PPL as described above for FIGS. **6**, **8**, **10** and **12**.

[0456] In some variations of a polymerization reactor, the plurality of cooling zones includes at least two cooling zones. In one variation, the plurality of cooling zones includes two cooling zones or three cooling zones.

[0457] For example, polymerization reactor **500** as depicted in FIG. **5** has three cooling zones **522**, **524** and **526**. In one variation, the three cooling zones are connected serially in the first 25% of the reaction length. In another variation, cooling zone **522** is configured to receive a mixture of bPL and the catalyst from the mixing zone at a rate of 3100 kg/hr; cooling zone **524** is configured to receive a mixture of the bPL, the catalyst and PPL produced in cooling zone **522** at a rate of 3100 kg/hr; and cooling zone **526** is configured to receive a mixture of the bPL, the catalyst, the PPL produced in cooling zone **522**, and PPL produced in cooling zone **524** at a rate of 3100 kg/hr.

[0458] In certain embodiments, the first 25% of the reaction length is a shell and a tube heat exchanger. In one variation, the shell may be configured to circulate a heat transfer fluid to maintain a constant temperature in reaction length **502**. In another variation, the tube heat exchanger is configured to remove heat produced in the first reaction zone.

[0459] With reference again to FIG. **5**, polymerization reactor **500** further includes end conversion zone **528** connected to plurality of cooling zones **520**. In some variations, the end conversion zone is configured to receive a mixture of the bPL, the catalyst, and the PPL produced in plurality of cooling zones at a rate of 3100 kg/hr. In one variation, the end conversion zone has no cooling load.

[0460] In one variation, the polymerization reactor is a plug flow reactor or a shell-and-tube reactor.

[0461] The one or more polymerization reactors used in the methods described herein may be constructed of any suitable material compatible with the polymerization. For example, the polymerization reactor may be constructed from stainless steel or high nickel alloys, or a combination thereof.

[0462] In some embodiments, the polymerization process comprises a plurality of polymerization reactors, and the polymerization catalyst is introduced only into the first reactor in the series. In other embodiments, the polymerization catalyst is added separately to each of the reactors in the series. For example, referring again to FIG. **4A**, depicted is a polymerization process comprising two CSTR in series, wherein polymerization catalyst is introduced to the first CSTR, and polymerization catalyst is separately introduced to the second CSTR. In other embodiments, a single plug flow reactor (PFR) is used, and polymerization catalyst is introduced at the beginning of the reactor, while in other embodiments polymerization catalyst is introduced separately at a plurality of locations along the length of the PFR. In other embodiments, a plurality of PFR is used, and polymerization catalyst is introduced at the beginning of the first PRF. In other embodiments, polymerization catalyst is introduced at the beginning of each PFR used, while in still other embodiments polymerization catalyst is introduced separately at a plurality of locations along the length of each PFR.

[0463] The polymerization reactor may comprise any suitable mixing device to mix the polymerization reaction mixture. Suitable mixing devices may include, for example, axial mixers, radial mixers, helical blades, high-shear mixers, or static mixers. Suitable mixing devices may comprise single or multiple blades, and may be top, bottom, or side mounted. The polymerization reactor may comprise a single mixing device, or multiple mixing devices. In some embodiments, a plurality of polymerization reactors is used, and each polymerization reactor comprises the same type of mixing device. In other embodiments, each polymerization reactor comprises a different type of mixing device. In yet other embodiments, some

polymerization reactors comprise the same mixing device, while others comprise different mixing devices

Preferred embodiments of polymerization sub-systems

[0464] In the preferred embodiments, distillation sub-system consists of (1) one or more polymerization reactors and (2) PPL purification/BPL recycle system.

Preferred BPL polymerization reactor

[0465] Polymerization of bPL can be performed in one or more reactors operating in series or parallel and in preferred embodiments the distillate stream consisting of essentially pure bPL (purity greater than 99.9wt%) with trace amounts of low- and high-boiling impurities (non limiting impurities are THF and Succinic Anhydride) is fed bPL Polymerization reactor. The bPL feed stream can be fed at the temperature of the bPL purification column overhead (50-100°C) or can be cooled to 20-50°C before being fed to the polymerization reactor.

[0466] The preferred combination of conditions for the polymerization of bPL include temperatures in the range 80-150°C, preferrably 120-145°C at pressures below or above atmospheric in the presence of polymerization initiator. The preferred initiators are quaternary amine and alkali metal salts of acrylic acid. Non limiting examples of polymerization initiators are Sodium Acrylate, Potassium Acrylate, Tetrabutylammonium Acrylate. The molar ratio of polymerization initiator to bPL is from 1:20000 to 1:100, preferably from 1:15000 to 1:500, preferably from 1:10000 to 1:1000, and most preferably from 1:8000 to 1:1500.

[0467] In such preferred embodiments, solid polymerization initiator is mixed with fresh bPL stream before the reactor; a high shear mixer can be used to achieve good mixing of bPL with initiator. In another embodiment, solid polymerization initiator is mixed with recycled bPL stream before the reactor; a high shear mixer can be used to achieve good mixing of bPL with initiator. In another embodiment, polymerization reactor if fed directly into the

polymerization reactor; optionally, an educator can be used to effectively mix solid initiator with all or part of bPL feed at the inlet to the reactor.

[0468] During polymerization of bPL to form PPL Acrylic Acid that acts as chain transfer agent can be formed in-situ. In some embodiments small amounts of acrylic acid can be fed to polymerization reactor to control molecular weight of PPL. To avoid radical polymerization of acrylic acid, radical polymerization inhibitors such as phenothiazine (PTZ) can be fed to the polymerization reactor. The concentration of radical polymerization inhibitor in the reactor is maintained at 50-500 ppm (by weight); preferred inhibitor concentration is in the range from 150 to 250 ppm.

[0469] If the plurality of polymerization reactors are operating in series, bPL can be fed to the first reactor only or bPL feed can be split between reactors in series. If the plurality of polymerization reactors are operating in series, a polymerization initiator can be fed to the first reactor only or initiator can be fed to each of the reactors in series.

[0470] In one of the preferred embodiments, polymerization of bPL can be conducted in one or more Continuous Stirred Tank Reactors (CSTR) operating in series. The polymerization reaction is exothermic and heat of the reaction can be removed by means known in the art such as an internal heat exchanger or jacket, an external heat exchanger (reaction mixture is circulated through external heat exchanger and cooled stream is returned to the reactor), evaporative cooling (reactor is equipped with attached condenser: bPL is evaporated from the reactor, condensed in the condenser, and cooled bPL stream is returned to the reactor). The reactors can be operated at atmospheric pressure, below atmospheric pressure, above atmospheric pressure.

[0471] In another preferred embodiment, polymerization of bPL can be conducted in one or more Loop Reactors operating in series. The reactors can be operated at or above atmospheric pressure. The temperatures of the surfaces in contact with the reaction mixture

containing bPL and PPL are kept at temperatures that prevent precipitation of PPL (PPL melting point is at about 70-80°C)

[0472] In another preferred embodiment, polymerization of bPL is conducted in the reactor system consisting of one or more CSTR or Loop Reactors followed by one or more Plug Flow Reactors (PFR). The temperatures of the surfaces in contact with the reaction mixture containing bPL and PPL are kept at temperatures that prevent precipitation of PPL (PPL melting point is at about 70-80°C)

[0473] The concentration of PPL in the stream exiting the reaction system (bPL conversion) is greater than 40wt%, preferably greater than 60wt%, preferably greater than 75wt%. The conversion of bPL can be greater than 80%, greater than 90%, greater than 95%, or greater than 99%. The stream exiting bPL polymerization system is fed forward to PPL purification and bPL recycle system. In one embodiment, polymerization reactor product stream consists of about 80wt% PPL, about 20wt% bPL, and polymerization initiator incorporated into PPL molecules.

Preferred PPL purification /BPL recycle system

[0474] The polymerization reactor product consisting of PPL product and unreacted bPL is fed forward to PPL purification and bPL recycle system. In preferred embodiments bPL can be separated from PPL in one or more flash evaporators operating under vacuum, or one or more Wiped Film Evaporators (WFE) operating under vacuum, or a combination thereof. To avoid decomposition of bPL within this system, surface temperatures in contact with bPL are kept below 200°C, preferably below 180°C, most preferably below 160°C. Recovered bPL is fed back to the polymerization reactor. Purified PPL contains less than 0.5wt% bPL, preferably less than 0.25wt% bPL, preferably less than 0.1wt% bPL, and preferably concentration of bPL in PPL product is less than 100 ppm. Most preferably PPL is fed forward to thermolysis reaction system for production of Acrylic Acid or pelletized for storage or shipment.

BPL Conversion

[0475] In some variations, between 5% and 100%, between 10% and 100%, between 20% and 100%, between 30% and 100%, between 40% and 100%, between 50% and 100%, between 60% and 100%, between 70% and 100%, between 80% and 100%, between 90% and 100, or between 95% and 100% of the bPL is converted to PPL in the polymerization process.

[0476] In some variations, bPL is partially converted to PPL in the polymerization process. For example, in some variations, complete conversion of bPL to PPL is greater than or equal to 75%, and partial conversion of bPL to PPL is less than 75%. In other variations, complete conversion of bPL to PPL is greater than or equal to 80%, and partial conversion of bPL to PPL is less than 80%. In other variations, complete conversion of bPL to PPL is greater than or equal to 85%, and partial conversion of bPL to PPL is less than 85%. In yet other variations, complete conversion of bPL to PPL is greater than or equal to 90%, and partial conversion of bPL to PPL is less than 90%. In yet other variations, complete conversion of bPL to PPL is greater than or equal to 95%, and partial conversion of bPL to PPL is less than 95%. In one variation, complete conversion of bPL to PPL is greater than or equal to 99%, and partial conversion of bPL to PPL is less than 99%.

[0477] In other variations, partial conversion is between 30% and 90%; between 40% and 90%, between 50% and 90%; or between 60% and 90%.

[0478] In some variations, the polymerization process comprises a plurality of polymerization reactors, and the conversion of bPL to PPL in each reactor is between 5% and 100%, between 10% and 100%, between 20% and 100%, between 30% and 100%, between 40% and 100%, between 50% and 100%, between 60% and 100%, between 70% and 100%, between 80% and 100%, between 90% and 100, or between 95% and 100% of the bPL is converted to PPL.

[0479] In some variations, the polymerization process comprises a plurality of polymerization reactors, and the conversion of bPL to PPL over the entire polymerization process is between 5% and 100%, between 10% and 100%, between 20% and 100%, between 30% and 100%, between 40% and 100%, between 50% and 100%, between 60% and 100%, between 70% and 100%, between 80% and 100%, between 90% and 100, or between 95% and 100% of the bPL is converted to PPL.

[0480] In one variation, two reactors are operated in series, and the conversion of bPL to PPL in each reactor is between 10% and 100%.

[0481] As described above in FIGS. **9-13**, in some embodiments of the methods to produce PPL as described herein, the bPL is completely converted to PPL. In other embodiments, the bPL is partially converted to PPL.

BPL Conversion

[0482] Without wishing to be bound by any theory, the polymerization of bPL to PPL proceeds quickly when the concentration of reactants is high and the concentration of products is low. As the reaction progresses to produce more products, the driving force for conversion is reduced. This phenomenon leads reactors which perform full conversion to be larger than those that perform partial conversion. Thus, in certain embodiments, the polymerization conditions and reactor size are selected such that conversion of bPL to PPL is partial (for example, 70% conversion), and a bPL/PPL separation device (for example, a WFE or distillation column) is used to recycle reactants back to the inlet of the reactor. Without wishing to be bound by any theory, this may avoid the requirements of a relatively large reactor while still generating a relatively pure product. In addition, the unreacted bPL is removed, which may make the handling of PPL easier. In the case where no PPL is isolated, removal of bPL reduces the possibility of other products forming during the thermolysis reaction

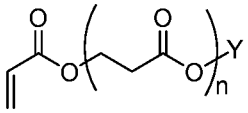
PPL Product Stream

[0483] In some embodiments, the production system/production process can produce at least about 2000 kg/hr PPL, at least about 2500 kg/hr PPL, at least about 3000 kg/hr PPL, at least about 3050 kg/hr PPL, or at least about 3500 kg/hr PPL, at least about 3638 kg/hr PPL, at least about 4000 kg/hr PPL, at least about 5000 kg/hr PPL, at least about 1000 kg/hr PPL, at least about 20000 kg/hr PPL, or at least about 35000 kg/hr PPL. In some embodiments, the production system/production process can produce about 2000 kg/hr PPL, about 2500 kg/hr PPL, about 3000 kg/hr PPL, about 3500 kg/hr PPL, about 3638 kg/hr PPL, about 4000 kg/hr PPL, about 5000 kg/hr PPL, about 1000 kg/hr PPL, about 20000 kg/hr PPL, or about 35000 kg/hr PPL. In some embodiments, the production system/production process can produce between 2000 kg/hr PPL and 3500 kg/hr PPL, between 2500 kg/hr PPL and 3500 kg/hr PPL, between bout 3000 kg/hr PPL and 3500 kg/hr PPL, between 2000 kg/hr PPL and 35000 kg/hr PPL, between 2500 kg/hr PPL and 35000 kg/hr PPL, between 3000 kg/hr PPL and 35000 kg/hr PPL, between 3500 kg/hr PPL and 35000 kg/hr PPL, between 3638 kg/hr PPL and 35000 kg/hr PPL, between 4000 kg/hr PPL and 35000 kg/hr PPL, between 5000 kg/hr PPL and 35000 kg/hr PPL, between 1000 kg/hr PPL and 35000 kg/hr PPL, or between 20000 kg/ PPL and 35000 kg/hr PPL.

[0484] In some embodiments, the production system/production process can produce at least about 25 kmol/hr PPL, at least about 30 kmol/hr PPL, at least about 40 kmol/hr PPL, at least about 42 kmol/hr PPL, or at least about 50 kmol/hr PPL. In some embodiments, the mass fraction of PPL in the PPL product stream in the production system/production process after polymerization can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.982, and at least about 0.99. In some embodiments, the mole fraction of PPL in the PPL product stream of the production system/production process after polymerization can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.984, and at least about 0.99. The remainder of the PPL product stream can include unreacted

bPL (in mole fraction of at most about 0.02, at most about 0.015, or at most about 0.011), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, at most about 0.005, or at most about 0.004,) and left over solvent (e.g., THF) and leftover carbonylation catalyst or components thereof (in at most about 1000 ppm). The PPL product stream can then receive thermolysis processing to form GAA. In some embodiments, the PPL product stream of the production system/production process can have a temperature between about 50-150°C, between about 110-150°C, or about 145°C. In some embodiments, the PPL product stream of the production system/production process can be at a pressure of at least about 0.001 bar, about 0.001-1 bar, or at least about 0.005 bar.

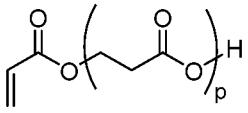
[0485] In certain embodiments, a method is provided for the production (e.g., integrated production) of a composition comprising PPL chains of Formula (**B**):



(**B**)

where *n* is an integer from 10 to about 1,000 and Y is either –H or a cation,

comprising the step of polymerizing bPL in the presence of a chain transfer agent selected from the group consisting of: a compound of Formula (**C**):



(**C**)

or a salt thereof, or a mixture of any two or more of these, where *p* is from 0 to 9. In certain embodiments, the composition further comprises PPL.

[0486] In certain embodiments, the PPL composition formed is characterized in that at least 90%, 95%, 99%, 99.5%, 99.8 or 99.9% of the polymer chains in the composition have an acrylate end group.

[0487] In certain embodiments, the PPL composition formed is characterized in that at least 90%, 95%, 99%, 99.5%, 99.8 or 99.9% of the polymer chains in the composition are of Formula (**B**).

[0488] In certain embodiments, *n* is, on average in the polypropiolactone composition, between 10 and 50, or between 50 and 100, or between 100 and 150, or between 150 and 250, or between 250 and 350, or between 350 and 500.

[0489] In some embodiments, the system described herein is configured to produce polypropiolactone with an average molecular weight between 800 g/mol and 100000 g/mol, between 500 g/mol and 70000 g/mol, between 1000 g/mol and 60000 g/mol, or between 1500 g/mol and 40000 g/mol. In some embodiments, the molecular weight is number average molecular weight, while in other embodiments, the molecular weight is weight average molecular weight.

[0490] In certain embodiments, the PPL composition is characterized in that it has a polydispersity index (PDI) of less than 10.

[0491] In certain embodiments, the PPL composition is characterized in that it has a PDI less than 8, or less than 5, or less than 3, or less than 2.5, or less than 2.0.

Cobalt/Ion Removal from PPL

[0492] In some embodiments, the PPL product stream is treated to reduce the concentration of cobalt and/or ions. The cobalt may be a cobalt ion or uncharged cobalt, or a combination thereof. The ions may be cobalt ions or non-cobalt ions.

[0493] In certain variations, the cobalt is a cobalt ion. The cobalt may be from decomposition of the carbonylation catalyst, residual catalyst components which comprise cobalt, or residual catalyst, or combinations thereof. For example, in some embodiments, the carbonylation catalyst decomposes to produce Co^{-1}, Co, Co^{+}, Co^{2+}, or Co^{3+}, or combinations

thereof. Thus, in some embodiments, the cobalt is a cobalt ion, while in other embodiments the cobalt is not a cobalt ion.

[0494] In some variations, at least some ions are removed from the PPL product stream. In some variations, the ions comprise metal ions. In other embodiments, the ions comprise non-metal ions. In yet other embodiments, the ions comprise both metal and non-metal ions. As discussed above, in certain variations, the ions comprise cobalt ions. The ions may be from decomposition of the carbonylation catalyst, residual catalyst components which comprise ions, residual catalyst, or ions produced as byproducts of the carbonylation reaction, or combinations thereof. For example in some embodiments, the carbonylation catalyst decomposes to produce Co^{-1}, Co^{+}, Co^{2+}, Co^{3+}, or Al^{3+}, or combinations thereof. In other embodiments, ions produced as byproducts of the carbonylation reaction include acetate ($CH_3C(O)O^-$) or acrylate ($CH_2=CHC(O)O^-$), or a combination thereof.

[0495] In certain embodiments, the step of treating the PPL product stream to remove at least a portion of cobalt and/or ions comprises ion exchange of cobalt and/or ions using ion exchange materials. In some embodiments, it may be possible to use an ion exchange resing for the ion exchange material. The ion exchange materials may be cationic, anionic, amphoteric, Lewis basic, Lewis acidic, or may comprise chelating groups. In certain embodiments, the ion exchange material may be a cation exchanger. In certain embodiments, functional groups on the cation exchange materials may be selected from: $–SO_3$, PO_3^{2-}, –COOH, $–C_6H_4OH$, –SH, $–AsO_3$, or $–SeO_3$, or combinations of two or more of these. In certain embodiments, functional groups on the cation exchange materials comprise $–SO_3$.

[0496] In certain embodiments, the ion exchange material may be an anion exchanger. In certain embodiments, functional groups on the anion exchange materials may be selected from: $–N^+(alkyl)_3$, $–N^+(CH_3)_3$, $–N^+(CH_3)_2C_2H_4OH$, $–N^+(CH_3)_2C_2H_5$, $–P^+(alkyl)_3$, $-P^+(aryl)_3$,–$P^+(C_4H_9)_3$, or $–P^+(Ph)_3$, or combinations of two or more of these. In certain embodiments,

functional groups on the anion exchange materials comprise $-N^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(aryl)_3$.

[0497] In certain embodiments where the step of treating the PPL product stream to separate cobalt and/or ions comprises ion exchange, the process entails both anion exchange and cation exchange. In certain embodiments the anion and cation exchange are performed concomitantly. In certain embodiments, the anion and cation exchange are performed sequentially. In certain embodiments, the anion exchange is performed first followed by cation exchange. In certain embodiments, the cation exchange is performed first followed by anion exchange. In certain embodiments, an organic ion exchange resin may prove useful in the separation step comprises an organic ion exchange resin. The general characteristics and properties of such resins are the same as previously described.

[0498] In various aspects, the bead size may be widely distributed, or may be very narrow, so-called mono-disperse resins. In embodiments where catalyst is removed from the PPL product stream by ion exchange, the ion exchange material can be contacted with the PPL product stream by any conventional method. This includes, but is not limited to: flowing the PPL product stream through a fixed bed of a solid ion exchange material (i.e. in the form of beads, granules or other particles); flowing the PPL product stream through a fluidized bed of adsorbent, flowing the PPL product stream through fabrics, meshes, or filtration plates comprising the ion exchange material, or slurrying the PPL product stream with the ion exchange material (typically followed by filtration, centrifugation, sedimentation or the like to remove the ion exchange material from the PPL product stream). In embodiments where the PPL product stream is flowed through a packed column of ion exchange material, it may be desirable to provide a plurality of such columns in parallel with a provision to switch the flow from one to another periodically. Thus when one column of ion exchange material becomes

saturated with cobalt and/or ions removed from the PPL product stream, it can be switched out of the flow path and the flow diverted to a fresh column---in certain embodiments, the interval of time from when a column is placed in the flow path to when it is switched out of the flow path corresponds to the "first time interval" recited in the methods described herein.

[0499] Where an ion exchange material is used to remove cobalt and/or ions from the PPL product stream, the inventive methods may include a subsequent step of removing the cobalt and/or ions from the ion exchange material. Such removal methods are well known in the art and typically involve contacting the ion exchange resin with a strong solution of a salt, the anion or cation of which will displace the adsorbed component from the ion exchange material.

[0500] In certain variations, the cobalt is Co^{-1}, Co, Co^{+}, Co^{2+}, or Co^{3+}, or a combination thereof. In some embodiments, the PPL product stream prior to cobalt removal has a cobalt concentration between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, between 0.05 mM and 0.2 mM, or between 0.07 mM and 0.15 mM. In some embodiments, the cobalt concentration of the permeate prior to cobalt removal is about 0.01 mM, about 0.03 mM, about 0.06 mM, about 0.09 mM, about 0.1 mM, about 0.13 mM, about 0.16 mM, about 0.19 mM, about 0.2 mM, about 0.23 mM, about 0.26 mM, about 0.29 mM, or about 0.3 mM. In one embodiment, the cobalt concentration of the PPL before cobalt removal is about 0.1 mM.

[0501] Thus, in some embodiments, the concentration of cobalt in the PPL product stream before contacting the ion exchange resin is between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, between 0.05 mM and 0.2 mM, or between 0.07 mM and 0.15 mM.

[0502] In some embodiments, the concentration of cobalt in the PPL product stream after contacting the ion exchange resin is between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM

and 0.015 mM. In one variation, the concentration of cobalt in the PPL product stream after contacting the ion exchange resin is 0.01 mM.

[0503] In some embodiments, at least some aluminum is removed from the PPL product stream. In certain variations, the aluminum is Al^{3+}. In some embodiments, the PPL product stream prior to aluminum removal has an aluminum concentration between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, or between 0.09 mM and 0.2 mM. In some embodiments, the PPL product stream prior to aluminum removal has a aluminum concentration of about 0.01 mM, about 0.03 mM, about 0.06 mM, about 0.09 mM, about 0.1 mM, about 0.13 mM, about 0.16 mM, about 0.19 mM, about 0.2 mM, about 0.23 mM, about 0.26 mM, about 0.29 mM, or about 0.3 mM. In one embodiment, the aluminum concentration of the PPL product stream before aluminum removal is about 0.1 mM.

[0504] Thus, in some embodiments, the concentration of aluminum in the PPL product stream before contacting the ion exchange resin is between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, between 0.05 mM and 0.2 mM, or between 0.07 mM and 0.15 mM.

[0505] In some embodiments, the concentration of aluminum in the PPL product stream after contacting the ion exchange resin is between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM and 0.015 mM. In one variation, the concentration of aluminum in the PPL product stream after contacting the ion exchange resin is 0.01 mM.

Solid PPL

[0506] In some embodiments, the production system/production process described herein further comprises a PPL stream processing system configured to receive the PPL product stream and produce solid PPL. For example, in one embodiment, the PPL product stream is

fed into at least one inlet of a PPL stream processing system, and solid PPL exits at least one outlet of the PPL stream processing system. The PPL stream processing system may be configured to produce solid PPL in any suitable form. For example, in some embodiments, the PPL stream processing system is configured to produce solid PPL in pelleted form, flaked form, granulated form, or extruded form, or any combinations thereof. Thus, solid PPL flakes, solid PPL pellets, solid PPL granules, or solid PPL extrudate, or any combinations thereof, may exit the outlet of the PPL stream processing system. The PPL stream processing system may include one or more flaking devices, pelleting devices, extrusion devices, or granulation devices, or any combinations thereof.

Geographic Location

[0507] In certain embodiments, the production system/production process described herein produces a PPL product stream at a first location, the PPL product stream is processed to produce solid PPL, and the solid PPL is converted to a GAA product stream in a second location. In some embodiments, the first location and the second location are at least 100 miles apart. In certain embodiments, the first location and the second location are between 100 and 12,000 miles apart. In certain embodiments, the first location and the second location are at least 250 miles, at least 500 miles, at least 1,000 miles, at least 2,000 or at least 3,000 miles apart. In certain embodiments, the first location and the second location are between about 250 and about 1,000 miles apart, between about 500 and about 2,000 miles apart, between about 2,000 and about 5,000 miles apart, or between about 5,000 and about 10,000 miles apart. In certain embodiments, the first location and the second location are in different countries. In certain embodiments, the first location and the second location are on different continents.

[0508] In certain embodiments, the solid PPL is transported from the first location to the second location. In some embodiments, the solid PPL is transported a distance of more than 100 miles, more than 500 miles, more than 1,000 miles, more than 2,000 miles or more than

5,000 miles. In certain embodiments, the solid PPL is transported a distance of between 100 and 12,000 miles, between about 250 and about 1000 miles, between about 500 and about 2,000 miles, between about 2,000 and about 5,000 miles, or between about 5,000 and about 10,000 miles. In some embodiments, the solid PPL is transported from a first country to a second country. In certain embodiments, the solid PPL is transported from a first continent to a second continent.

[0509] In certain embodiments, the solid PPL is transported from the North America to Europe. In certain embodiments, the solid PPL is transported from the North America to Asia. In certain embodiments, the solid PPL is transported from the US to Europe. In certain embodiments, the solid PPL is transported from the US to Asia. In certain embodiments, the solid PPL is transported from the Middle East to Asia. In certain embodiments, the solid PPL is transported from the Middle East to Europe. The solid PPL may be transported by any suitable means, including, for example, by truck, train, tanker, barge, or ship, or any combinations of these. In some embodiments, the solid PPL is transported by at least two methods selected from truck, train, tanker, barge, and ship. In other embodiments, the solid PPL is transported by at least three methods selected from truck, train, tanker, barge, and ship.

[0510] In some embodiments, the solid PPL is in the form of pellets, flakes, granules, or extrudate, or any combination thereof. In some variations, the solid PPL is converted to a GAA product stream using the thermolysis reactor as described herein. In some variations, the solid PPL is fed into an inlet of the thermolysis reactor and is converted to a GAA product stream. In other embodiments, the solid PPL is converted to molten PPL, and the molten PPL is fed into an inlet of the thermolysis reactor as described herein and converted to a GAA product stream.

Acrylic Acid Production system/production process

[0511] Polypropiolactone (PPL) can generally be converted to acrylic acid (AA) according to the following scheme:



PPL AA

[0512] In certain embodiments, the polypropiolactone produced undergoes thermolysis continuously (e.g. in a fed batch reactor or other continuous flow reactor format). In certain embodiments, the continuous thermolysis process is linked to a continuous polymerization process to provide acrylic acid at a rate matched to the consumption rate of the reactor.

Thermolysis Reactors

[0513] In some embodiments, the thermolysis reactor is a fluidized bed reactor. Inert gas may be used to fluidize inert solid heat transfer medium (HTM), and polypropiolactone is fed to the reactor. In some variations, the polypropiolactone may be fed to the reactor in molten form, for example, via a spay nozzle. The molten form may help facilitate the dispersion of polypropiolactone inside the reactor.

[0514] The reactor may be equipped with a cyclone that returns HTM solid back to the reactor. The inert gas, glacial acrylic acid, and higher boiling impurities (such as succinic anhydride and acrylic acid dimer) are fed from the cyclone to a partial condenser where impurities are separated. For example, the condenser may be used to condense the high boiling impurities, and such impurities can then be purged from the reactor as a residual waste stream.

[0515] Glacial acrylic acid with the inert gas may be fed to a second condenser where the glacial acrylic acid and the inert gas are separated. A liquid glacial acrylic acid stream is output from the second condenser, and the inert gas is output as a separate stream that may be returned

back to the reactor to fluidize the heat transfer solid. The glacial acrylic acid stream may be used for condensation/absorption and then storage.

[0516] The residual waste stream purged from the reactor may include, for example, high boiling organics (or organic heavies), for example, resulting from the polymerization catalyst and succinic anhydride, as well as the cationic and anionic carbonylation catalyst species if carbonylation catalyst was not separated prior to the thermolysis reactor. In some embodiments, the high boiling organics (or organic heavies) may include any compounds which are not acrylic acid. In certain embodiments, the high boiling organics (or organic heavies) may include any compounds which remain in the bottoms stream after condensing the acrylic acid in the glacial acrylic acid production system/production process. In some embodiments, the high boiling organics (or organic heavies) may include succinic anhydride, polymerization catalyst, or carbonylation catalyst or components thereof (for example, organic compounds from the carbonylation catalyst). In some embodiments, the high boiling organics (or organic heavies) have a boiling point higher than acrylic acid.

[0517] In other embodiments, the thermolysis reactor is a moving bed reactor. Polypropiolactone is fed into a moving bed reactor as a solid and glacial acrylic acid exits the reactor as a vapor stream and is then condensed.

Conditions

[0518] In some variations, the operating temperature in the thermolysis reactor is from about 150 °C to about 300 °C, from about 150 °C to about 200 °C, from about 150 °C to about 250 °C, from about 175 °C to about 300 °C, from about 200 °C to about 250 °C, from about 225 °C to about 275 °C, from about 250 °C to about 300 °C, from about 200 °C to about 300 °C, from about 200 °C to about 400 °C, or from about 200 °C to about 500 °C. In some variations, operating temperature is the average temperature of the contents of the reactor.

[0519] In some variations, the operating pressure in the thermolysis reactor is from about 0.01 atmospheres to about 500 atmospheres (absolute), from about 0.01 atmospheres to about 10 atmospheres (absolute), from about 0.01 atmospheres to about 50 atmospheres (absolute), from about 1 atmosphere to about 10 atmospheres (absolute), from about 1 atmosphere to about 50 atmospheres (absolute), from about 1 atmosphere to about 100 atmospheres (absolute), from about 10 atmospheres to about 50 atmospheres (absolute), from about 10 atmospheres to about 100 atmospheres (absolute), from about 50 atmospheres to about 100 atmospheres (absolute), from about 50 atmospheres to about 200 atmospheres (absolute), from about 100 atmospheres to about 200 atmospheres (absolute), from about 100 atmospheres to about 250 atmospheres (absolute), from about 200 atmospheres to about 300 atmospheres (absolute), from about 200 atmospheres to about 500 atmospheres (absolute), or from about 250 atmospheres to about 500 atmospheres (absolute).

[0520] In a particularly preferred embodiment the PPL stream from a bPL polymerization system enters primary thermolysis reactor, either in solid or liquid phase at a temperature between 100°C and 320°C, and absolute pressure between 1mmHg and 5000mmHg. One of many methods may provide heat transfer input, for example internal coils, external heat exchanger with a pump-around loop from and back to the primary reactor, or a baffled jacket on the walls of the reactor. Alternatively, a high temperature liquid or gas that that does not significantly affect the reaction chemistry may be introduced to maintain desired reaction temperature and separated downstream. Depending upon time and temperature residence time for complete conversion may vary from a few seconds to 24 hours or more. Mixing of the contents of the reactor may also improve mass and heat transfer.

[0521] Preferably the thermolysis conditions and arrangement will minimize the loss of PPL. to polyacrylic acid. Representative ways of avoiding polyacrylic acid production include the use of a depolymerization catalyst to decrease required reaction severity to decrease the

reaction rate of acrylic acid to polyacrylic acid relative to PPL to acrylic acid; the use of high concentrations of radical polymerization inhibitor; and/or means to minimize the concentration of acrylic acid in the liquid phase.

[0522] A continuous PPL thermolysis design (continuous, equal mass flows in and out of the primary reactor) can minimize the concentration of acrylic acid in the liquid phase, which lowers the reaction rate of acrylic acid to polyacrylic acid relative to that of PPL to acrylic acid. Removing vapors from the headspace of the primary reactor will lower the acrylic acid partial pressue in the headspace of the reactor and its liquid contents. Sparging with an inert gas, preferably continuously will further reduce the concentration of acrylic acid in the reactor's liquid contents. Withdrawal of liquid effluent stream and any other nonvolatile components may also be desired to manage accumulation of polyacrylic acid. These may be directed to a second thermolysis reactor, to waste treatment, or to a reactive distillation to convert the considerable PPL in the stream to volatile species such as acrylic acid and short-chain PPL oligomers. The vapor effluent from this distillation operation can flow back to the primary reactor, or be mixed with the vapor effluent from the primary reactor.

[0523] The vapor effluent from the various forms and number of suitable thermolysis reactor preferably, before going to product storage, undergoes condensation; passes in vapor phase to a distillation operation to remove higher-boiling and/or lower-boiling impurities before condensation; goes to condensation, then to a distillation in liquid phase to remove higher-boiling and/or lower-boiling impurities and then condensation. In another embodiment the the vapor effluent is condensed internally and isolated from the products that are non-volatile before undergoing further purification via distillation before storage or goes directly to product storage. Limiting the temperature of any liquid-phase acrylic acid is known to limit yields to polyacrylic acid. Preferably radical polymerization inhibitor shall be use in all liquid

phase acrylic acid. The bottoms from a distillation operation shall optimally be returned to the primary thermolysis reactor for further thermolysis, but may be disposed of as well.

[0524] In some variations, the thermolysis process is operated under an oxygen and water free atmosphere. For example, in certain variations, the amount of oxygen present in the thermolysis reactor is less than 1 wt%, less than 0.5 wt%, less than 0.01 wt%, or less than 0.001 wt %. In certain variations, the amount of water present in the thermolysis reactor is less than 1 wt%, less than 0.5 wt%, less than 0.01 wt%, or less than 0.001 wt%.

Glacial Acrylic Acid

[0525] In some variations, glacial acrylic acid produced according to the systems and methods described herein has a purity of at least 98%, at least 98.5%, at least 99%, at least 99.1%, at least 99.2%, at least 99.3%, at least 99.4%, at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%; or between 99% and 99.95%, between 99.5% and 99.95%, between 99.6% and 99.95%, between 99.7% and 99.95%, or between 99.8% and 99.95%.

[0526] In other variations, acrylic acid produced according to the systems and methods described herein is suitable to make high molecular weight polyacrylic acid. In certain variations, acrylic acid produced according to the systems and methods described herein may have a lower purity, such as 95%. Thus, in one variation, the acrylic acid has a purity of at least 95%.

[0527] In yet other variations, the glacial acrylic acid has:

(i) a cobalt level of less than 10 ppm, less than 100 ppm, less than 500 ppm, less than 1 ppb, less than 10 ppb, or less than 100 ppb; or

(ii) an aluminum level of less than 10 ppm, less than 100 ppm, less than 500 ppm, less than 1 ppb, less than 10 ppb, or less than 100 ppb; or

(iii) a β-propiolactone level of less than 1 ppm, less than 10 ppm, less than 100 ppm, less than 500 ppm, less than 1 ppb, or less than 10 ppb;

(iv) an acrylic acid dimer level of less than 2000 ppm, less than 2500 ppm, or less than 5000 ppm; or

(v) a water content of less than 10 ppm, less than 20 ppm, less than 50 ppm, or less than 100 ppm,

or any combination of (i) to (v).

[0528] Unlike known methods to produce glacial acrylic acid, acetic acid, furfurals and other furans are not produced and thus, are not present in the glacial acrylic acid produced.

[0529] Glacial acrylic acid may be used to make polyacrylic acid for superabsorbent polymers (SAPs) in disposable diapers, training pants, adult incontinence undergarments and sanitary napkins. The low levels of impurities present in the glacial acrylic acid produced according to the systems and methods herein help to facilitate a high-degree of polymerization to acrylic acid polymers (PAA) and avoid adverse effects from by-products in end applications. For example, aldehyde impurities in acrylic acid hinder polymerization and may discolor the polymerized acrylic acid. Maleic anhydride impurities form undesirable copolymers which may be detrimental to polymer properties. Carboxylic acids, e.g., saturated carboxylic acids that do not participate in the polymerization, can affect the final odor of PAA or SAP-containing products and/or detract from their use. For example, foul odors may emanate from SAP that contains acetic acid or propionic acid and skin irritation may result from SAP that contains formic acid. The reduction or removal of impurities from petroleum-based acrylic acid is costly, whether to produce petroleum-based crude acrylic acid or petroleum-based glacial acrylic acid. Such costly multistage distillations and/or extraction and/or crystallizations steps are generally employed (e.g., as described in U.S. Pat. Nos. 5,705,688 and 6,541,665).

GAA Production system/production process

[0530] In some embodiments, the production system/production process can produce at least about 25 kilo tons per annum ("KTA") glacial acrylic acid ("GAA"), at least about 160 KTA GAA, at least about 250 KTA GAA, or at least about 400 KTA GAA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, at least about 2500 kg/hr GAA, at least about 3000 kg/hr GAA, at least about 3025 kg/hr GAA, at least about 3500 kg/hr GAA, at least about 3638 kg/hr GAA, at least about 4000 kg/hr GAA, at least about 5000 kg/hr GAA, at least about 1000 kg/hr GAA, at least about 20000 kg/hr GAA, or at least about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 2000 kg/hr GAA, about 2500 kg/hr PPL, about 3000 kg/hr GAA, about 3500 kg/hr GAA, about 3638 kg/hr GAA, about 4000 kg/hr GAA, about 5000 kg/hr GAA, about 1000 kg/hr GAA, about 20000 kg/hr GAA, or about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce between 2000 kg/hr GAA and 3500 kg/hr GAA, between 2500 kg/hr GAA and 3500 kg/hr GAA, between bout 3000 kg/hr GAA and 3500 kg/hr GAA, between 2000 kg/hr GAA and 35000 kg/hr GAA, between 2500 kg/hr GAA and 35000 kg/hr GAA, between 3000 kg/hr GAA and 35000 kg/hr GAA, between 3500 kg/hr GAA and 35000 kg/hr GAA, between 3638 kg/hr GAA and 35000 kg/hr GAA, between 4000 kg/hr GAA and 35000 kg/hr GAA, between 5000 kg/hr GAA and 35000 kg/hr GAA, between 1000 kg/hr GAA and 35000 kg/hr GAA, or between 20000 kg/hr GAA and 35000 kg/hr GAA. In some embodiments, the production system/production process can produce at least about 25 kmol/hr GAA, at least about 30 kmol/hr GAA, at least about 35 kmol/hr GAA, at least about 40 kmol/hr GAA, at least about 42 kmol/hr, or at least about 50 kmol/hr GAA. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product

stream of the production system/production process can have a temperature between about 20-60°C, between about 30-50°C, or about 40°C. In some embodiments, the GAA product stream of the production system/production process can be at a pressure of at least about 0.5 bar, about 0.5-1.5 bar, or at least about 1 bar.

Polymerization Examples

Example 1

Batch bPL polymerization using sodium acrylate as initiator

[0531] Under nitrogen, a Parr reactor equipped with an ATR-IR sentinel was charged with 16.2 mg of sodium acrylate. The reactor was sealed and heated to 100°C. In a 50 mL stainless vessel, a mixture of 11.8 mg of phenothiazine and 25 g of beta-propiolactone was added under nitrogen. The vessel was sealed and connected to the reactor. The mixture of beta-propiolactone and phenothiazine was injected into the reactor containing sodium acrylate with 50 psi of CO pressure at 100 °C. The reaction was agitated to 500 rpm, and monitored by in-line IR. The plot of beta-propionate peak at 1836 cm-1 and poly(propiolactone) peak at 1739 cm-1 as a function of time is shown in Figure 17. After the temperature was stabilized, the reaction temperature was set to 145 °C. And the reaction was run for 5 hours, by which time, the reaction went to completion.

[0532] The polymer formed in the reactor was extracted with CHCl3. Volatiles were stripped off by a rotovap. The polymer was further dried under a high vacuum to yield 21.8 g of a white solid. The solid was analyzed by 1H NMR, TGA, SEC, and melt rheology. SEC of the isolated solid gave am Mn of 3710 and an Mw of 8740.

Example 2

Batch bPL polymerization using tetra(butylammonium) acrylate as initiator

[0533] Under nitrogen, a Parr reactor equipped with an ATR-IR sentinel was charged with 12.2 mg of tetrabutylammonium acrylate. The reactor was sealed and heated to 100°C. In a

50 mL stainless vessel, 25 g of beta-propiolactone was added under nitrogen. The vessel was sealed and connected to the reactor. Into the reactor containing tetrabutylammonium acrylate, beta-propiolactone was injected with 50 psi of CO pressure at 100°C. The reaction was agitated to 500 rpm, and monitored by in-line IR. The plot of beta-propionate peak at 1836 cm^{-1} and poly(propiolactone) peak at 1739 cm^{-1} as a function of time is shown in Figure 21. After the temperature was stabilized, the reaction temperature was set to 140°C. At 36 min after the bPL addition, the reaction reached around 89% conversion, and 25 mL of water was added with 100 psi of CO at 140°C. After hydrolyzing the remaining beta-propiolactone, the polymer was extracted with CH_2Cl_2. Volatiles were removed using a rotovap and high vacuum to yield 17.7 g of a white solid. The solid was analyzed by ^1H NMR, TGA and melt rheology.

Example 2

Polymerization production using plug-flow reactor arrangement

[0534] A plug-flow reactor, consisting of two jacketed static mixers of ½" OD X 24 ¾" length and ~60 mL volume, an 3-way nitrogen/feed inlet ball-valve and an outlet with a jacketed viscometer (Cambridge Viscosity ViscoPro 2000 with 372 sensor), type K thermocouple, ATIR IR probe (Mettler-Toledo DS AgX CompTM and ReactIRTM 15) and a 0-250 psig back-pressure regulator, was heated to 140°C and purged with nitrogen at ambient pressure. A feed mixture was prepared by combining 0.1670 g of sodium acrylate (milled, sieved to 100 mesh and dried at 130°C under vacuum, 0.001776 mol), 0.1536 g phenothiazine and 670 mL of □-propiolactone (~ 760 g, 10.6 mol, chilled to -20°C) in a one liter, pressure/vacuum rated GL45 bottle equipped with a magnetic stir-bar in a glove-box. The bottle was closed with a three port GL45 cap equipped with a dip-tube and 2-way, 1/8" ball-valve on one port, a 1/8" 2-way-ball valve with a 1 psi cracking-pressure check-valve on the second port and a 1/8" 3-way ball-valve with one Luer-Lock fitting on the third port. The mixture was stirred briefly to dissolve the phenothiazine and suspend the sodium acrylate. The

sealed bottle was removed from the glove-box, transported to the plug-flow reactor, immersed in a water/ice bath on top of a magnetic stirrer and connected via the three 1/8" compression fittings to a feed pump, a vent line (to a scrubber filled with 2% sulfuric acid) and a nitrogen needle-valve, respectively. The mixture was stirred at 400 rpm to keep the sodium acrylate suspended. The 2-way vent-valve was opened followed by switching the 3-way nitrogen/fill valve from closed to nitrogen and adjusting the nitrogen needle-valve to give a steady stream of bubbles in the scrubber. The feed valve was then opened followed by a prime valve on the feed pump (Eldex Optos 2SM, 0.01 – 10.00 mL/min) and the pump was turned on at a flow rate of 5.00 mL/min and allowed to run until the (Teflon FEP) line from the prime port to the scrubber showed that all bubbles had been ejected. The pump was then turned off, flow set to 0.50 mL/min, prime/feed 3-way ball-valve switched to feed, the reactor inlet 3-way ball-valve switched from nitrogen to feed and the pump turned back on.

[0535] After 4 hours, the reactor exit back-pressure regulator was adjusted from ambient pressure to 200 psig and both the viscometer and the ReactIR were turned on. After another hour and a half, the reactor was fully pressurized, the viscometer (70 cP, compensated to 120°C) and ReactIR (~95% conversion) readings were steady and product was collected into a one liter collection bottle which contained 300 mL of magnetically stirred water. After a further 22.5 hours, the feed mixture was nearly exhausted and a 20 mL portion of chloroform was added to the feed bottle via syringe and the Luer-Lock fitting on the nitrogen/fill 3-way ball-valve. When the feed bottle was nearly empty again, another 20 mL of chloroform was added. When that charge had been consumed, a further 500 mL of chloroform was added. A fresh receiving bottle was placed on the reactor exit and conditions maintained for another 21 hours when feed pump and circulating bath were turned off.

[0536] The crude product mixture from the first receiver bottle was transferred to a large blender with an additional 500 mL of water, blended until no particles > 5 mm were observed

and the solid collected by filtration, air-dried and then vacuum dried at 40°C for 20 hours to give 562.1 grams of solid PPL product. The mixture of PPL solution in chloroform and aqueous liquid from the second receiver bottle was separated, the chloroform phase washed with water, dried and concentrated to 300 mL by azeotropic distillation and diluted in 600 mL of 2-propanol. The resulting precipitate was collected by filtration, air dried and then dried in vacuo at 40°C for 2 hours to give 90.5 grams of colorless solid PPL product. The filtrate was stripped of volatiles on a rotary evaporator at 50°C to give 45.0 g of clear, colorless oil, which separated into liquid and solid upon cooling.

[0537] 1H NMR analysis suggested that solid from the first receiver was composed of 556 grams of PPL, with a molecular weight of ~ 1210 g/mol with small amount (6 grams) of 3-hydroxypropionic acid (3-HPA) resulted from the hydrolysis of bPL in water (the GPC results showed Mn = 275, Mw = 1530 and Mn/Mw = 5.56). The isolated solid from the second receiver contained 90 grams of PPL with a molecular weight of 2030 g/mol (the GPC results showed Mn = 328, Mw = 1900, Mw/Mn = 5.79.) and 0.5 grams of 3-HPA.

Polymerization Examples

Example 4

Batch Thermolysis of PPL to Acrylic Acid

[0538] A lab-scale batch thermolysis system consisting of a two-necked round-bottom glass flask of 25mL approximate internal volume (the reaction flask) was carried out. The reaction flask was equipped with an internal thermocouple and the top center opening in the flask was equipped with a short-path distillation apparatus. The short-path distillation apparatus consisted of a short path still (similar to Ace Glass item #6554-06) with an additional thermocouple to monitor vapor temperature, followed by a water-cooled condenser, and finally a four-armed "cow" product receiver in a dry ice/acetone-cooled dewar. The reaction flask was set in a fabric heating mantle, the power to which was controlled by a temperature controller

that receives feedback from the thermocouple inside the reaction flask. Additional heat was provided with electric heat tape, wrapped around the top of the reaction flask and the distillation apparatus. The top of the reaction flask and the bottom of the distillation apparatus were insulated. The fabric heating mantle was set above a magnetic stir plate, and a PTFE-coated stir bar was added to the reaction flask.

[0539] The tared reaction flask was charged with 90mg dry sodium acrylate, 5mg PTZ, and 4.995g of PPL produced from ring-opening polymerization of solvent-free bPL in the presence of sodium acrylate (at a concentration of 1mol per 6,000mol of bPL) and phenothiazine (at a concentration of 200 ppmw in bPL). In addition, the tared product receiver was pre-charged with 5mg PTZ (distributed among the four product arms). After system assembly, the product receiver was attached to a nitrogen and vacuum source, and the air was displaced with nitrogen. Next, the reactor contents were heated to 90degC to melt and begin stirring. The system was brought under vacuum to an absolute pressure of approximately 700torr, and the reactor temperature setpoint was set to 210degC. Internal reflux was observed inside the reaction flask within minutes. It took 8-10minutes to heat reactor contents up to 210degC. The moment the reactor contents reached 210degC is defined as t=0. The reactor contents were held at 210degC for 10minutes, at which point the reactor flask was mostly empty, save for a glassy darker solid and the stir bar.

[0540] It was later determined that the residual material in the reaction flask weighed 156mg. Four product samples were obtained—sample 129-098A contained material collectred until t=2minutes, 129-098B contained material collected between t=2minutes and t=8minutes, 129-098C contained material between t=8minutes and t=9minutes, and 129-098D contained collected material between t=9minutes and t=10minutes, when heat sources were shut off. The total product collected weighed 4.7816g. Next, each sample was pipetted from the cow to labeled vials, and samples were taken for 1H NMR (see figures 25-28). NMR analysis suggests

an average acrylic acid content in 129-098A of 94.4%, in 129-098B of 90.7%, in 129-098C of 90.6%, and in 129-098D of 92.5% by mass. The balance consists of di-acrylic acid ester and traces of other PPL oligomers where n>2.

Polymerization Examples

Example 4

Batch Thermolysis of PPL to Acrylic Acid

[0541] A lab-scale batch thermolysis system consisting of a two-necked round-bottom glass flask of 50mL approximate internal volume (the reaction flask). The reaction flask was equipped with an internal thermocouple and the top center opening in the flask is equipped with a distillation apparatus. The distillation apparatus consisted of two Vigreux columns in series oriented coaxially (each similar to Ace Glass item #6578-04), followed by an adapter with an additional thermocouple to monitor vapor temperature, followed by a water-cooled condenser, and finally a 50mL round-bottom product receiver in a dry ice/acetone-cooled dewar. The reaction flask was set in a fabric heating mantle, the power to which is controlled by a temperature controller that receives feedback from the thermocouple inside the reaction flask. Additional heat was provided with electric heat tape, wrapped around the top of the reaction flask and the distillation apparatus. The top of the reaction flask and the bottom of the distillation apparatus are insulated. The fabric heating mantle was set above a magnetic stir plate, and a PTFE-coated stir bar is added to the reaction flask.

[0542] The tared reaction flask was charged with 1000mg dry sodium acrylate, 20mg PTZ, and 19.162g of PPL produced from ring-opening polymerization of solvent-free bPL in the presence of sodium acrylate (at a concentration of 1mol per 6,000mol of bPL) and phenothiazine (at a concentration of 200ppmw in bPL). In addition, the tared product receiver was pre-charged with 5mg PTZ. After system assembly, the product receiver was attached to a nitrogen and vacuum source, and the air was displaced with nitrogen. Next, the reactor

contents were heated to 90degC to melt and begin stirring. The system was brought under vacuum to an absolute pressure of approximately 90torr, and the reactor temperature setpoint was set to 165degC. Internal reflux was observed inside the reaction flask within minutes. It took approximately 10minutes to heat reactor contents up to 165degC. The moment the reactor contents reached 165degC is defined as t=0. The reactor contents were held at 165degC for 40minutes, at which point the reactor flask was still easily mixed by the stir bar.

[0543] It was later determined the residual material in the reaction flask weighed 4.7186g. Product sample 129-108 consisted of all collected product, and weighed 14.6586g. Next, a sample was taken for 1H NMR (see figure 29). NMR analysis suggests an average acrylic acid content in 129-108_Dist of 99.7%. The balance consists of di-acrylic acid ester and traces of other PPL oligomers where n>2.

[0544] This application discloses several numerical ranges in the text and figures. The numerical ranges disclosed inherently support any range or value within the disclosed numerical ranges even though a precise range limitation is not stated verbatim in the specification because this invention can be practiced throughout the disclosed numerical ranges.

[0545] The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, systems and methods described herein are not intended to be limited to the embodiments shown, but are to be accorded the widest scope consistent with the principles and features disclosed herein. Finally, the entire disclosure of the patents and publications referred in this application are hereby incorporated herein by reference.

CLAIMS

What is claimed is:

1. 1. A process for producing acrylic acid from a source of β-propiolactone, comprising:

contacting a BPL feed stream comprising β-propiolactone with a polymerization initiator in a polypropiolactone reaction zone having at least one polymerization reactor that produces a polypropiolactone outlet stream comprising polypropiolactone and β-propiolactone; and,

passing at least a portion of the polypropiolactone outlet stream to an acrylic acid production zone comprising a thermolysis reactor that receives the at least a portion of the polypriolactone outlet stream and produces an acrylic acid stream comprising acrylic acid.

2. The process of claim 1wherein the source of the β-propiolactone in the BPL feed stream isfrom ethylene oxide and carbon monoxide produced by:

contacting input components comprising carbon monoxide feed, an ethylene oxide feed, and a catalyst recylce stream with a carbonylation catalyst and a solvent in a carbonylation reaction zone and producing a BPL outlet stream comprising β-propiolactone, ethylene oxide and carbonylation catalyst;

passing at least a portion the BPL outlet stream to a carbonylation catalyst recycling zone and separating said portion into i) BPL separation stream comprising a portion of the BPL outlet stream from which at least some carbonylation catalyst has been removed and ii) the recycle stream, comprising β-propiolactone, solvent, ethylene oxide, carbonylation catalyst, succinic anhydride, and acetaldehyde;

passing at least a portion of the recycle stream to the carbonylation reaction zone;

purifying at least a portion of the BPL separation stream in a BPL purification zone comprising at least one separator, wherein the BPL purification zone produces a purified BPL stream and rejects a portion of β-propiolactone and rejects solvent, ethylene oxide, and carbonylation catalyst, succinic anhydride and acetaldehyde in one or more rejction streams streams comprising at least one of β-propiolactone, solvent, ethylene oxide, and carbonylation catalyst, succinic anhydride and acetaldehyde; and,

passing at least a portion of the purified BPL stream to the polypropiolactone reaction zone.

3. The process of claim 1 or 2 wherein the polymerization initiator is selected from the group consisting of quaternary ammonium salts, alkali metal salts of carboxylic acids, ammonium acrylate, ammonium acetate, phosphonium acrylate, phosphonium salts, sodium acrylate, potassium acrylate, phosphonium acetate, tetra-n-butylammonium acrylate, sodium acetate, potassium acetate, tetra-n-butylammonium acetate, trimethylphenylammonium acrylate, trimethylphenylammonium acetate, or tetraphenyl phosphonium acrylate and a radical polymerization inhibitor is present in the polypropiolactone reaction zone.

4. The process of any of claims 1-3 wherein the radical polymerization inhibitor comprises phenothiazine preferably in a concentration of 50-500 ppmw and more preferably in a concentration of 150 to 250 ppm.

5. The process of any of claims 1-4 wherein the polypropiolactone reactor zone comprises a first polymerization reactor and a second polymerization reactor; the first polymerization reactor produces an intermediate mixture comprising polypropiolactone, β-

propiolactone and polymerization initiator; the intermediate mixture and additional polymerization initiator passes to the second polymerization reactor that produces at least a portion of the polypropiolactone outlet stream; and at least a portion of the polypropiolactone outlet stream comprises polypropiolactone, β-propiolactone, and polymerization initiator.

6. The process of claim 5 wherein polypropiolactone is separated from the portion of the polypropiolactone outlet stream produced by the second reaction zone in at least one of an evaporator, flash tank evaporator, wiped film evaporator, or a distillation apparatus.

7. The process of any of claims 1 - 6 wherein the polypropiolactone outlet stream comprises a solid polypropiolactone.

8. The process of any of claim 1-7 wherein the at least one polymerization reaction zone contains at least one of a continuous reactor, semi-batch reactor, a continuous-flow stirred-tank reactor, a loop reactor, or plug-flow reactor and acrylic acid reaction zone comprises a thermolysis reactor for receiving molten propiolactone and the thermolysis reactor is in the form of a continuous stirred tank reactor, plug flow reactor, wiped film evaporator, a moving bed reactor, kneader reactor, and fluidized bed reactor.

9. The process of any of claims 1- 8 wherein at least a portion of the acrylic acid stream is separated into (i) an acrylic acid stream comprises acrylic acid having a purity of at least 90%, and (ii) an organic heavies stream.

10. The process of any of claims 2-8 wherein the BPL purification zone produces an EO rejection stream as one of the rejection streams, said EO rejection stream comprising ethylene oxide and at least a portion of the EO rejection is passed to the carbonylation reaction zone.

11. The process of claim and of claims 2-10 wherein the BPL purification zone produces a solvent recovery stream as one of the EO rejection streams, said solvent recovery stream comprising solvent at least a portion of the solvent recovery stream is passed to the carbonylation reaction zone.

12. The process of nay of claims 2-11 wherein I) the carbonylation catalyst recycling zone comprises one or more membrane systems from which the catalyst recycle stream is recovered as a retentate and BPL separation stream is recovered as a permeate; and II) the BPL purification zone comprises a.) an EO recovery section comprising at least one distillation column that receives at least a portion of the BPL separation stream and produces an EO stream containing ethylene oxide that is passed to the carbonylation reactor and a solvent bottoms stream containing solvent and β-propiolactone, b.) a solvent recovery section comprising at least one distillation column that receives at least a portion of the solvent bottoms stream and produces a overhead recovered solvent stream comprising solvent that is passed to the carbonylation zone and a BPL bottoms stream comprising β-propiolactone, and c.) a BPL concentration section comprising at least one distillation column that receives the BPL bottoms stream and produces an bottoms rejection stream and produces the the purified BPL as an overhead stream.

13. The process of any of claims 2-12 wherein the carbonylation catalyst is at least one of a cobalt-aluminum catalyst; a carbonyl cobaltate in combination with an aluminum porphyrin compound, a carbonyl cobaltate in combination with an aluminum salen compound, a carbonyl cobaltate in combination with an aluminum salophen compound, and Al(TPP)Co(CO)4).

14. The process of any of claim 2-13 wherein the carbonylation catalyst is at least partially dissolved in a catalyst solvent and the solvent comprises at least one an ether, a

hydrocarbon, tetrahydrofuran, hexane, 2,5-dimethyl tetrahydrofuran, sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, propyl acetate, butyl acetate, 2-butanone, cyclohexanone, toluene, difluorobenzene, dimethoxy ethane, acetone, and methylethyl ketone.

15. The process of any of claims 2-14 wherein the carbonylation reaction zone: includes reactor operating conditions of temperatures of from -20°C to 160°C and pressures of from 100 psig to 5000 psig; at least one reactor selected from the group consisting of a continuous reactor or a semi-batch reactor a continuous-flow stirred-tank reactor or a loop reactor; and produces β-propiolactone with a selectivity of at least 90% and preferably at least 99%

16. The process of claim 2-15 wherein the BPL outlet stream satisfies on a mass fraction basis the condition of having; at least 0.1 and at most 0.4 β-propiolactone; at least 0. and at most 0.9 solvent; at least 0.005 and at most 0.07 ethylene oxide; between 0.0005 to 0.001 of carbon monoxide; at least 0.0001 and at most 0.005 catalyst; at least 0.0001 and at most 0.06 acetaldehyde; or at least 0.0001 and at most 0.06 succinic anhydride.

17. The process of any of claims 2-16 wherein the BPL concentration section includes a vacuum column and the purified BPL stream is recovered as a vacuum column overhead stream having a β-propiolactone purity of at least 99% and preferabaly at least 99.5% and most preferably 99.9%.

19. A process for producing acrylic acid from ethylene oxide and carbon monoxide, comprising:

contacting carbon monoxide feed, an ethylene oxide feed, an CO overhead stream and a BPL recycle stream with a carbonylation catalyst and a solvent in a carbonylation reaction zone and producing a BPL outlet stream comprising β-propiolactone, solvent, ethylene oxide, carbon monoxide, carbonylation catalyst, acetaldehyde, and succinic anhydride;

passing at least a portion of the BPL outlet stream to a CO/EO separator and recovering i.) the CO separator overhead stream wherein the CO separator overhead stream comprises ethylene oxide and carbon monoxide and ii.) an CO separator bottoms stream comprising β-propiolactone, solvent, carbonylation catalyst, acetaldehyde, succinic anhydride, and ethylene oxide;

passing at least a portion of the CO separator overhead stream to the carbonylation reaction zone;

passing at least a portion the CO separator bottoms stream to a membrane separation section of a carbonylation catalyst recycling zone and separating said at least a portion of the CO separator bottoms stream into i) a BPL recycle stream comprising a retentate containing separated carbonylation catalyst, solvent, and β-propiolactone and ii) a BPL separation stream comprising a permeate containing β-propiolactone, solvent, acetaldehyde, succinic anhydride, ethylene oxide and carbonylation catalyst;

passing at least a portion of the BPL recycle stream to the carbonylation reaction zone;

passing at least a portion of the BPL separation stream to a BPL purification zone comprising at least one separation zone that separates the BPL separation stream

into a solvent recycle stream comprising solvent, and a purified BPL stream comprising β-propiolactone and carbonylation catalyst;

passing at least a portion of the purified BPL stream and a polymerization initiator to a polypropiolactone reaction zone having at least one polymerization reactor that contacts the at least a portion of the purified BPL stream with the polymerization initiator and produces a polypropiolactone outlet stream comprising polypropiolactone and β-propiolactone;

passing at least a portion of the polypropiolactone outlet stream to a PPL/BPL processing zone having at least one separation zone to produce i.) an PPL/BPL overhead stream that increases the concentration of β-propiolactone relative to the polypropiolactone outlet stream and ii) a PPL/BPL separator bottoms stream that comprises polypropiolactone;

passing at least a portion of the PPL/BPL overhead stream to the polyproprionate reaction zone;

passing at least a portion of the a PPL/BPL bottoms stream to an acrylic acid production zone comprising a thermolysis reactor that receives the at least a portion of the a polypropiolactone outlet stream and produces an acrylic acid stream; and,

separating at least a portion of the acrylic acid stream in a separator into (i) acrylic acid stream comprising acrylic acid having a purity of at least 90%, and (ii) an organic heavies stream.

18. The process of claim 17 wherein the acrylic acid stream has a acrylic acid purity of greater than 99.5% and comprises glacial acrylic acid.

19. The process of any of claims 17-18 wherein the at least one polymerization reactor produces polypropiolactone at a polypropiolactone conversion of at least 50%.

20. The process of of any of claims 17-19 wherein the at least one separation zone in the PPL/BPL processing zone comprises at least one flash tank and/or at least one evaporator comprising a wiped film evaporator, thin film evaporator, or falling film evaporator; and the the CO separator is a flash tank.

21. The process of any of claims 17-20 wherein the carbonylation reactor zone operates at a temperature between 30°C and 160°C and a pressure between 100 psig and 5000 psig the at least one distillation column operates at or below atmospheric pressure and at a temperature of less than 120°C.

22. The process of of any of claims 17-21 wherein the solvent recycle stream comprises solvent and less than 15 wt% of β-propiolactone, ethylene oxide, carbon monoxide, acetaldehyde, or succinic anhydride, or any combinations thereof and wherein the purified BPL stream comprises (i) β-propiolactone and (ii) less than 1 wt% of solvent, ethylene oxide, carbon monoxide, acetaldehyde, or succinic anhydride, or any combinations thereof.

23. A process for producing acrylic acid from ethylene oxide and carbon monoxide, comprising:

contacting carbon monoxide feed, an ethylene oxide feed, an CO overhead stream and a BPL recycle stream with a carbonylation catalyst and a solvent in a carbonylation reaction zone and producing a BPL outlet stream comprising β-propiolactone, solvent, ethylene oxide, carbon monoxide, carbonylation catalyst, acetaldehyde, and succinic anhydride;

passing at least a portion of the BPL outlet stream to a CO separator and recovering i.) the CO overhead stream wherein the CO overhead stream comprises ethylene oxide and carbon monoxide and ii.) a CO bottoms stream comprising β-propiolactone, solvent, carbonylation catalyst, acetaldehyde, succinic anhydride, ethylene oxide and carbon monoxide;

passing at least a portion of the CO overhead stream to the carbonylation reaction zone;

passing at least a portion the CO bottoms stream to a membrane separation section of a carbonylation catalyst recycling zone and separating said at least a portion of the CO bottoms stream into i) a BPL recycle stream comprising a retentate containing separated carbonylation catalyst, solvent and β-propiolactone and ii) a BPL separation stream comprising a permeate containing β-propiolactone, solvent, acetaldehyde, succinic anhydride, ethylene oxide, carbon monoxide, and carbonylation catalyst;

passing at least a portion of the BPL recycle stream to the carbonylation reaction zone;

purifying the BPL separation stream in a BPL purification zone comprising at least one distillation column that further separates the BPL separation stream into a solvent recycle stream comprising solvent and a purified BPL stream comprising β-propiolactone;

passing at least a portion of the purified BPL stream and a polymerization initiator to a polypropiolactone reaction zone having at least one polymerization reactor that contacts the at least a portion of the purified BPL stream with the polymerization

initiator and produces a polypropiolactone outlet stream comprising polypropiolactone and β-propiolactone; and,

passing at least a portion of the polypropiolactone outlet stream to an acrylic acid production zone comprising a thermolysis reactor that receives the at least a portion of the polypropiolactone outlet stream and produces an acrylic acid stream; and,

separating at least a portion of the acrylic acid stream in a condenser into (i) an acrylic acid stream comprises acrylic acid having a purity of at least 90%, and (ii) an organic heavies stream.

24. The process of claim 23 wherein the acrylic acid stream has an acrylic acid purity of greater than 99.5% and comprises glacial acrylic acid.

25. The process of any of claims 23-24 wherein the at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone first passes to a polypropiolactone purification zone, comprising a PPL ion exchange zone comprising a resin column that purifies the at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone so that it comprises at least 90 wt% of polypropiolactone and removes an ionic species stream comprising cationic carbonylation catalyst species and anionic carbonylation catalyst species; and wherein at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone passes from the polypropiolactone purification zone first passes to a polypropiolactone processing zone before passing to the acrylic acid production zone and the polypropiolactone processing zone converts the at least a portion of the purified polypropiolactone outlet stream that passes to the acrylic acid production zone to solid form.

26. The process of any of claims 23-25 wherein a.) at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone passes from the polypropiolactone purification zone to a PPL/BPL processing zone before passing to the acrylic acid production zone and the PPL/BPL processing zone has at least one separation zone to produce i.) an overhead stream that increases the concentration of β-propiolactone in the at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone and ii.) a PPL/BPL bottoms stream that comprises polypropiolactone and b.) a condensate ion exchange zone comprising a resin column receives at least a portion of the organic heavies and separates the organic heavies into an heavies output stream and an ionic species stream comprising cationic carbonylation catalyst species and anionic carbonylation catalyst species.

27. A method for continuously producing polypropiolactone, comprising:

continuously feeding β-propiolactone into a first reactor;

continuously feeding polymerization initiator into the first reactor;

producing a first mixture comprising polypropiolactone and unreacted β-propiolactone in the first reactor,

wherein the first reactor comprises:

a β-propiolactone inlet to receive the β-propiolactone from a β-propiolactone source,

a first initiator inlet to receive the initiator from a initiator source, and

a first mixture outlet to output the first mixture; and

transferring the first mixture from the first reactor to a second reactor;

optionally feeding additional initiator from the initiator source to the second reactor;

producing a second mixture comprising polypropiolactone and unreacted β-propiolactone,

wherein the second reactor comprises:

a mixture inlet to receive the first mixture from the first reactor,

optionally, a second initiator inlet to receive the additional initiator from the initiator source, and

a second mixture outlet to output the second mixture.

28. A solid transportable polymer composition, comprising:

at least 95 wt% of polypropiolactone;

less than 1 ppm of cobalt or ions thereof;

less than 10 ppm of aluminum or ions thereof;

less than 10 ppm acetic acid;

less than 500 ppm of tetrahyrofuran; and

less than 10 ppm of succinic anhydride

less than 10 ppm β-propiolactone

less than 6000 ppm water

29. A β-propiolactone composition, comprising:

at least 99 wt% of β-propiolactone;

less than 10 ppm of cobalt or ions thereof;

less than 10 ppm of aluminum or ions thereof;

less than 300 ppm of acetic acid;

less than 500 ppm of succinic anhydride;

less than 500 ppm of tetrahyrofuran;

less than 100 ppm Ethylene Oxide;

less than 100 ppm acetaldehyde; an average molecular weight of polypropiolactone of between 800 and 100000 g/mol.

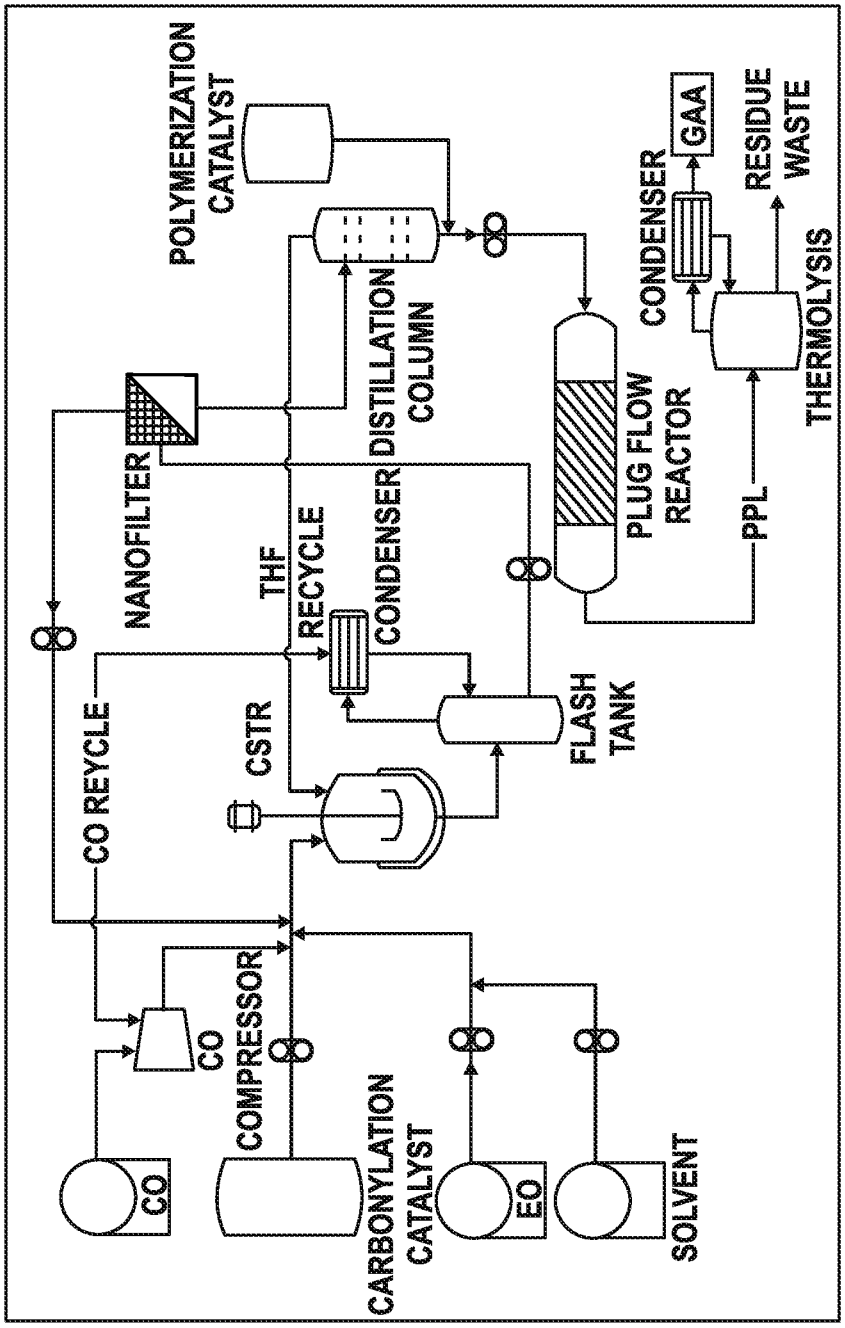

POLYMERIZATION CATALYST
DISTILLATION COLUMN
NANOFILTER
THF RECYCLE
CONDENSER
PLUG FLOW REACTOR
CONDENSER
GAA
RESIDUE WASTE
THERMOLYSIS
PPL
CO REYCLE
CSTR
FLASH TANK
CO COMPRESSOR
CO
CARBONYLATION CATALYST
EO
SOLVENT

FIG. 1

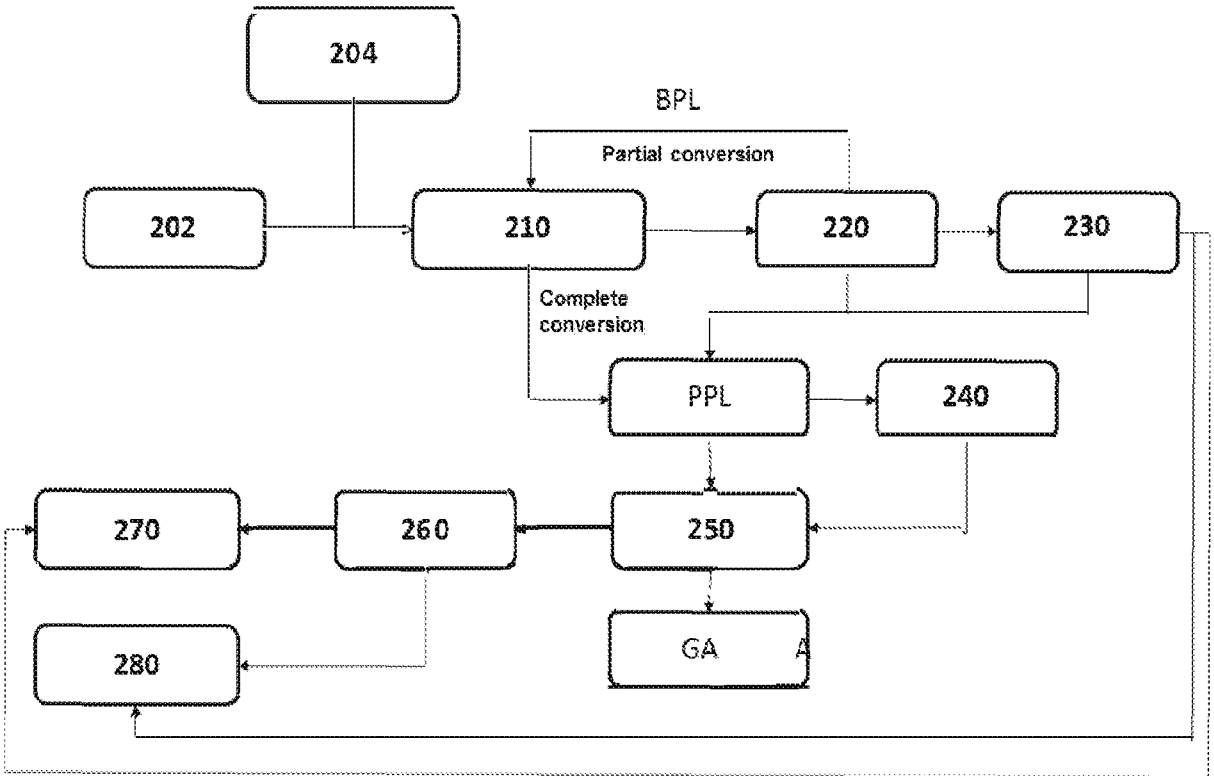

204
BPL
Partial conversion
202
210
220
230
Complete conversion
PPL
240
270
260
250
280
GA

FIG. 2

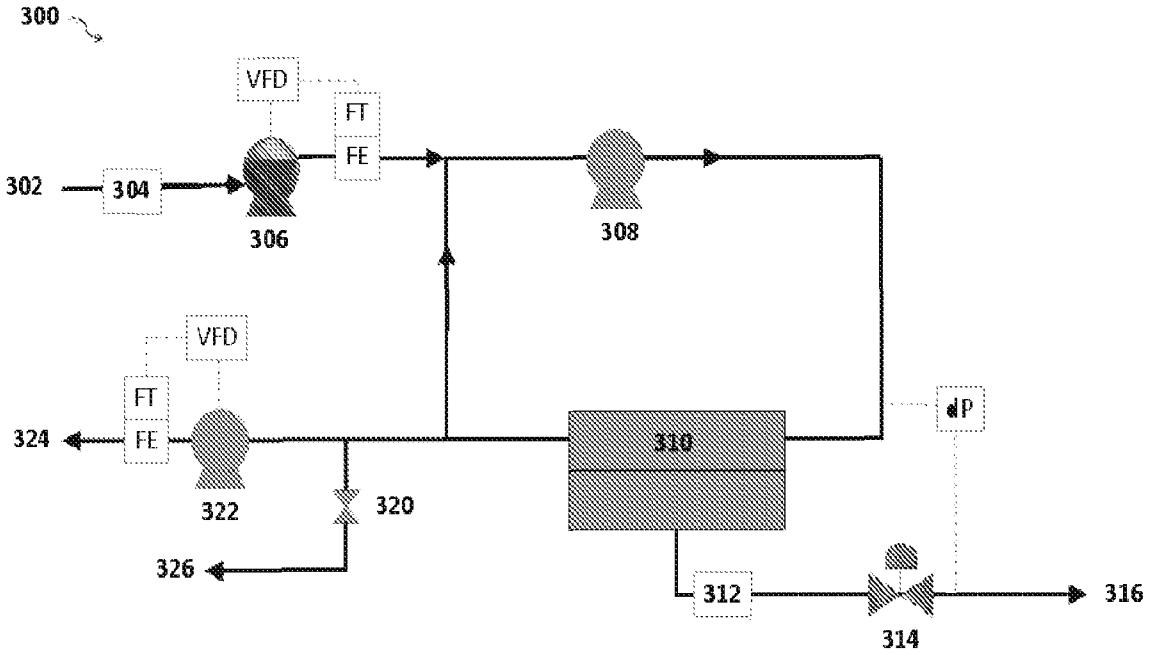

300
VFD
FT
FE
302
304
306
308
VFD
FT
FE
324
322
320
326
310
dP
312
314
316

FIG. 3

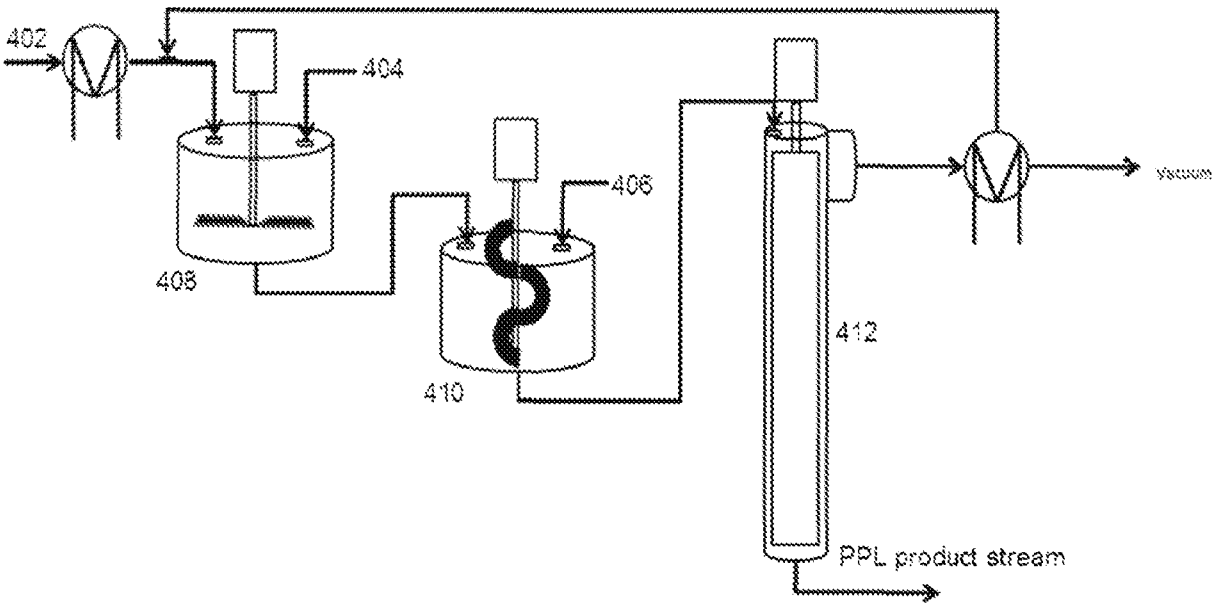

402
404
406
408
410
412
PPL product stream

FIG. 4A

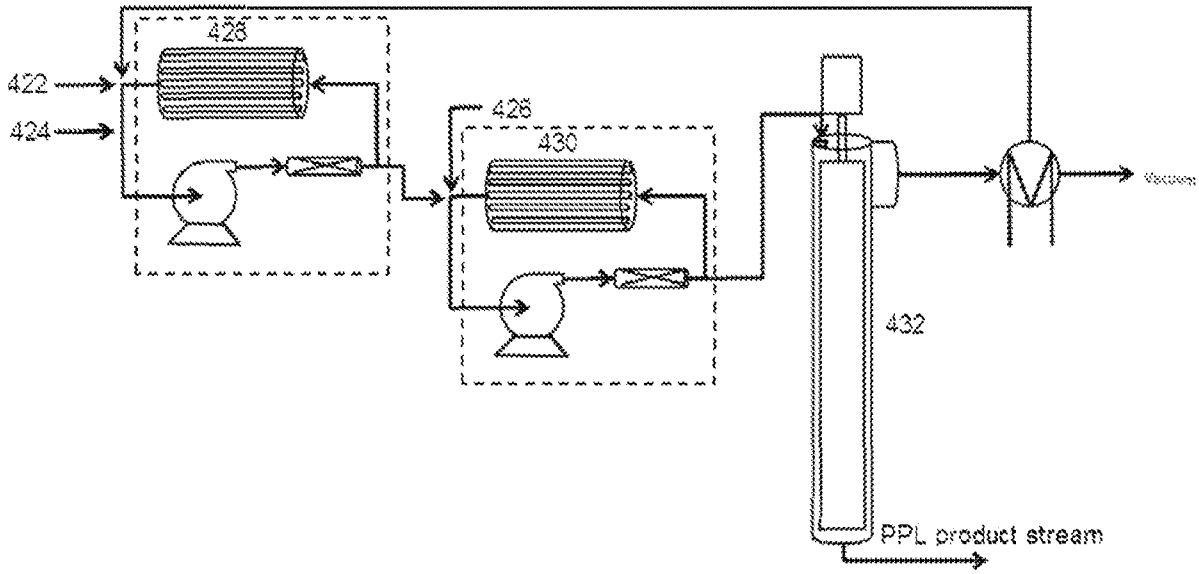

428
422
424
426
430
432
PPL product stream

FIG. 4B

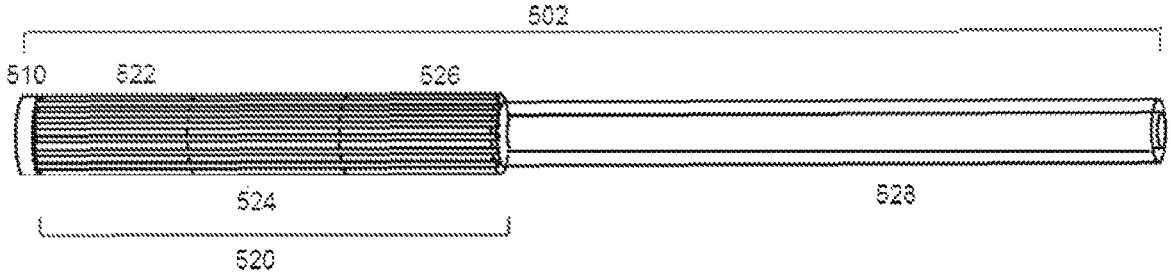

502
510
522
526
524
528
520

FIG. 5

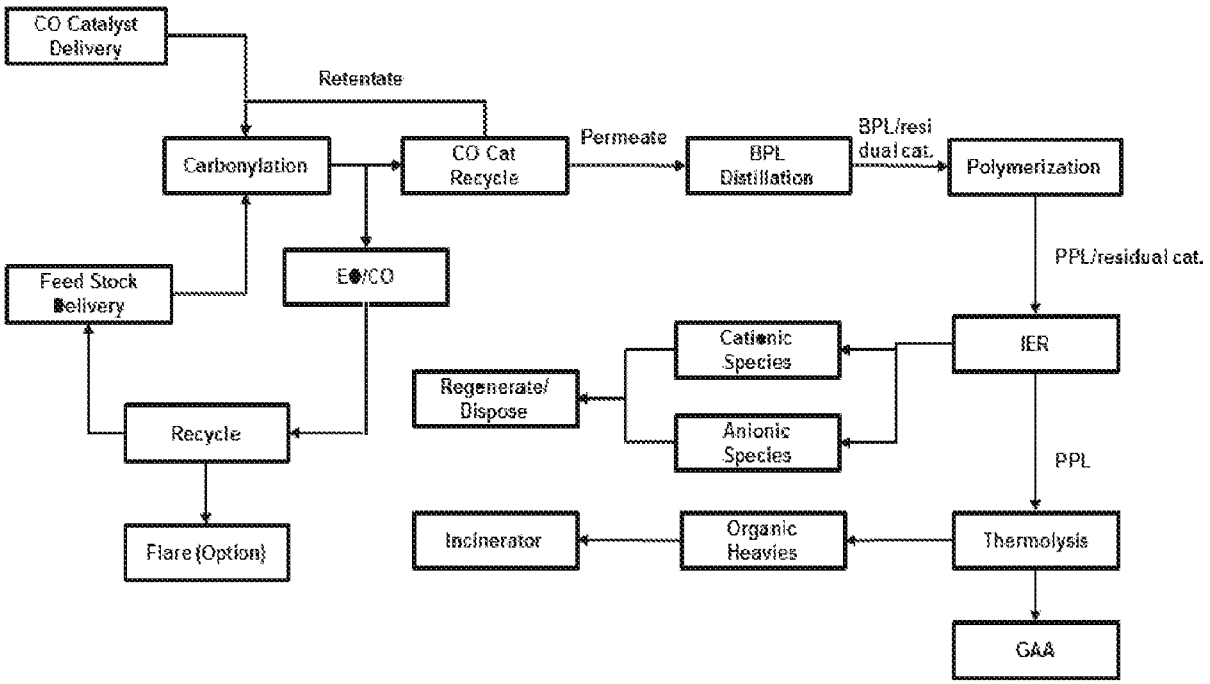

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
PPL/residual cat.
Feed Stock Delivery
EO/CO
Cationic Species
IER
Regenerate/ Dispose
Anionic Species
Recycle
PPL
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
GAA

FIG. 6

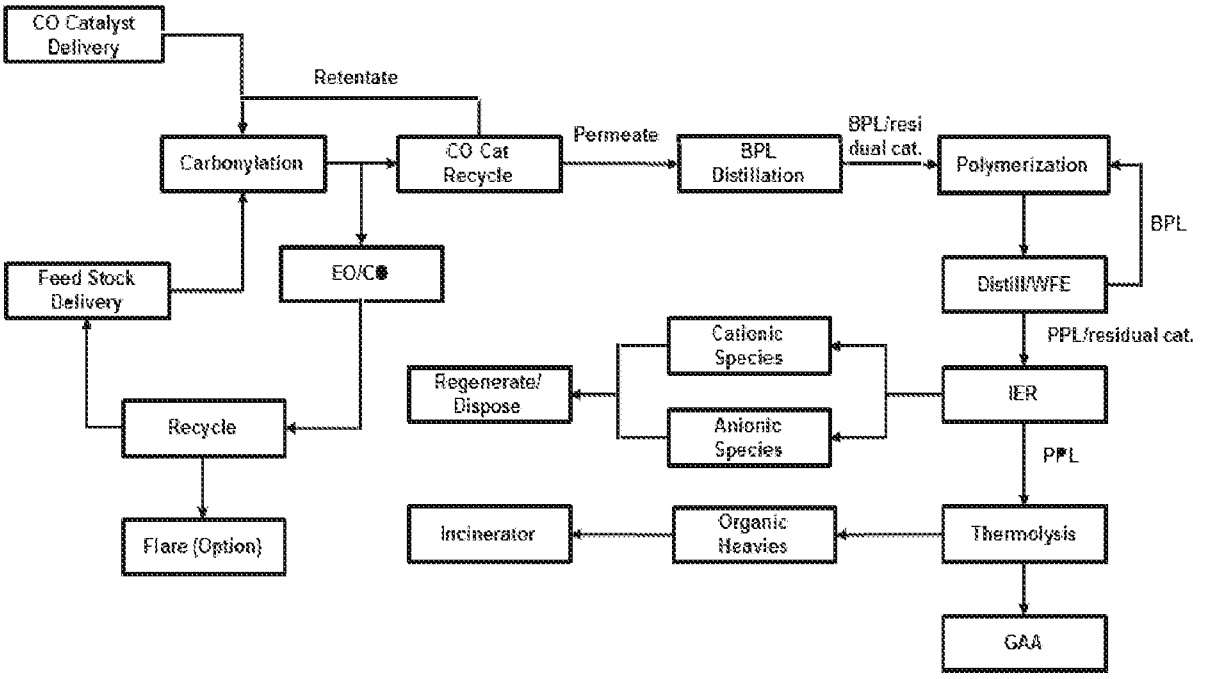

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Cationic Species
Regenerate/ Dispose
IER
Recycle
Anionic Species
PPL
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
GAA

FIG. 7

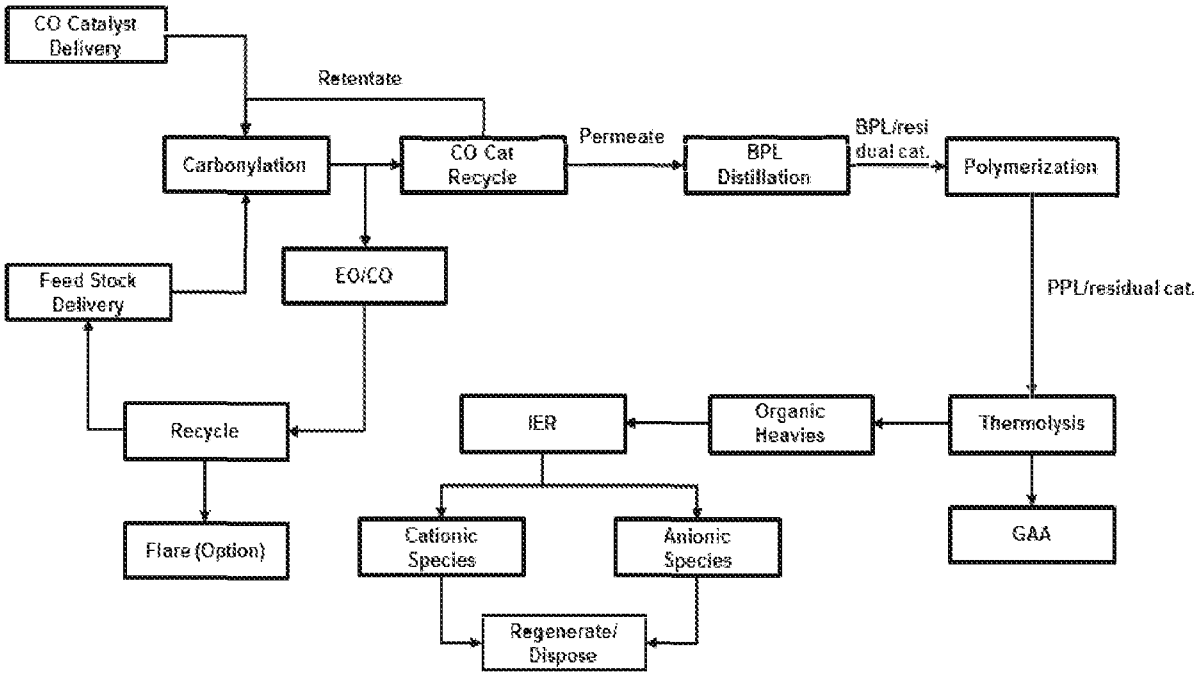

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
Feed Stock Delivery
EO/CO
PPL/residual cat.
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose

FIG. 8

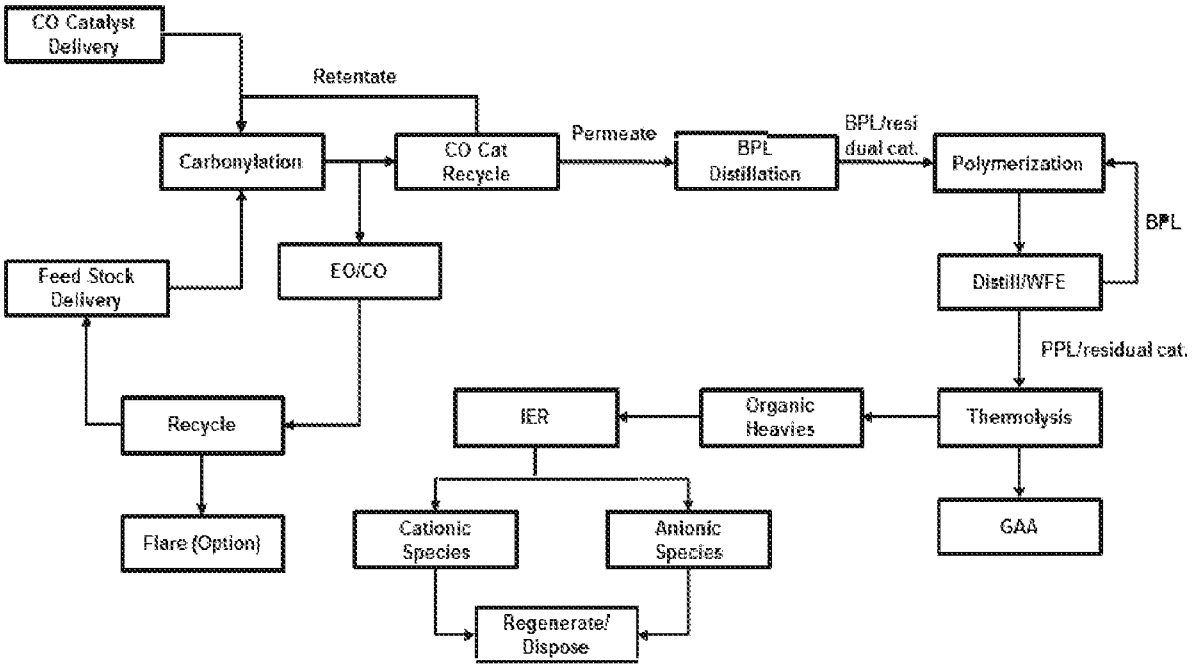

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose

FIG. 9

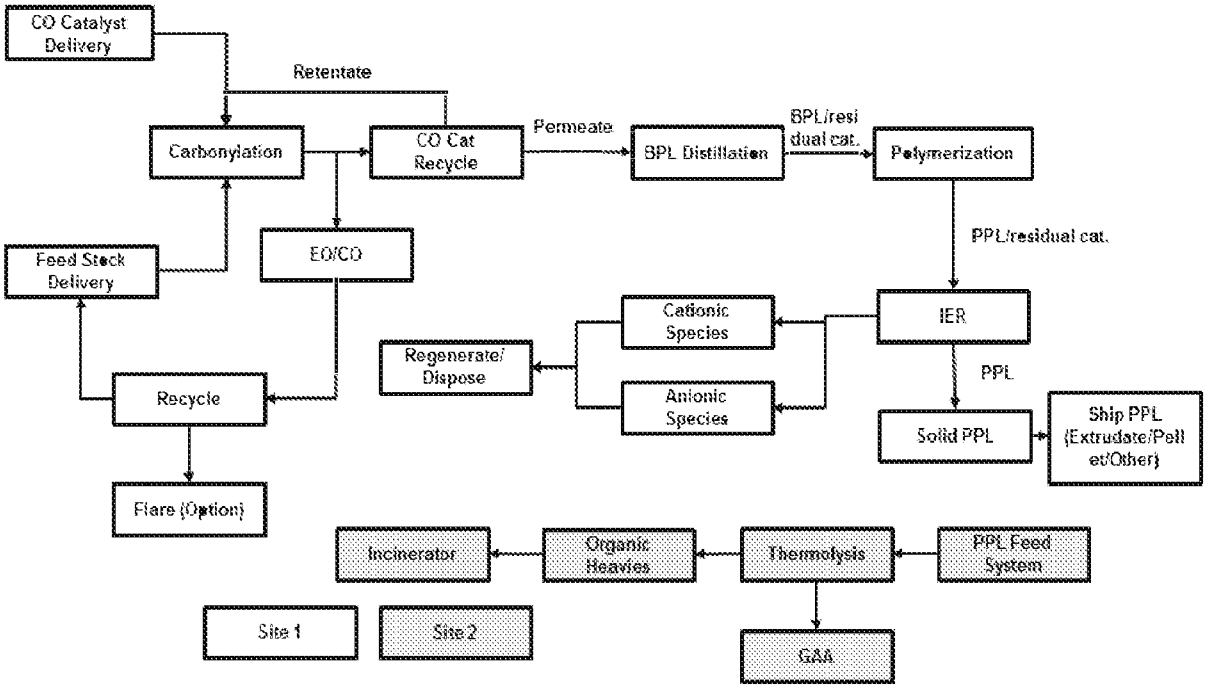

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
PPL/residual cat.
Feed Stock Delivery
EO/CO
Cationic Species
IER
Regenerate/ Dispose
Anionic Species
PPL
Recycle
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
PPL Feed System
Site 1
Site 2
GAA

FIG. 10

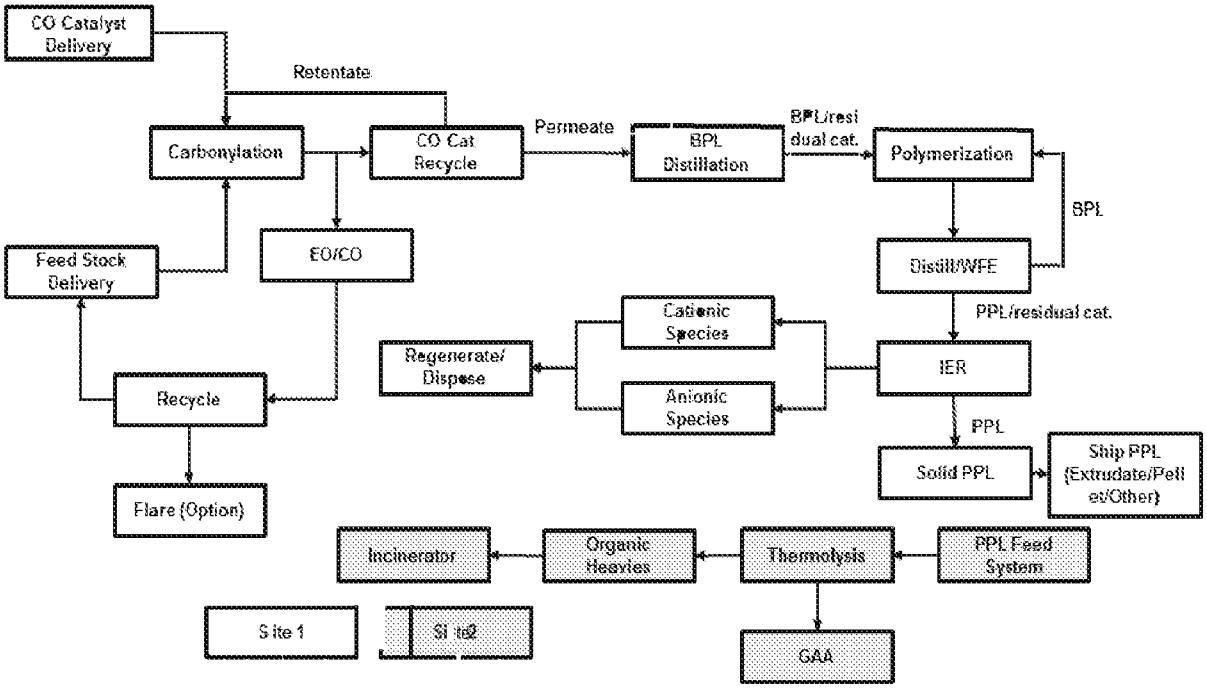

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Cationic Species
Regenerate/ Dispose
IER
Anionic Species
PPL
Recycle
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
PPL Feed System
Site 1
Site 2
GAA

FIG. 11

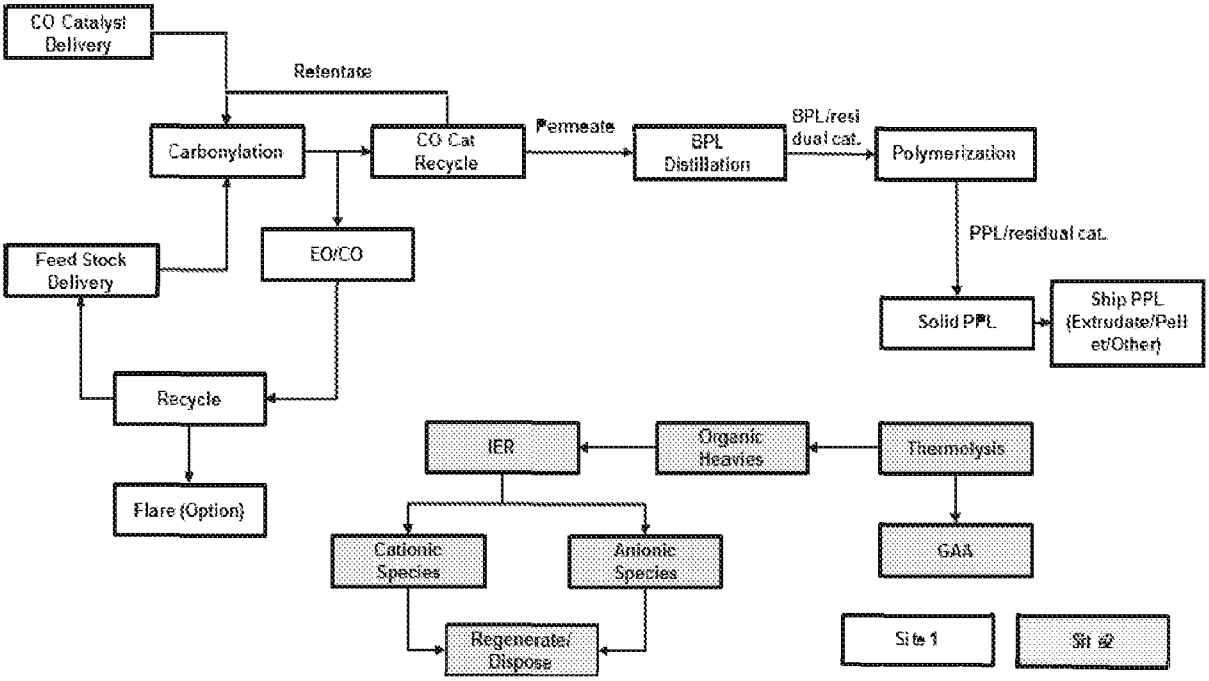

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
PPL/residual cat.
Feed Stock Delivery
EO/CO
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose
Site 1
Site 2

FIG. 12

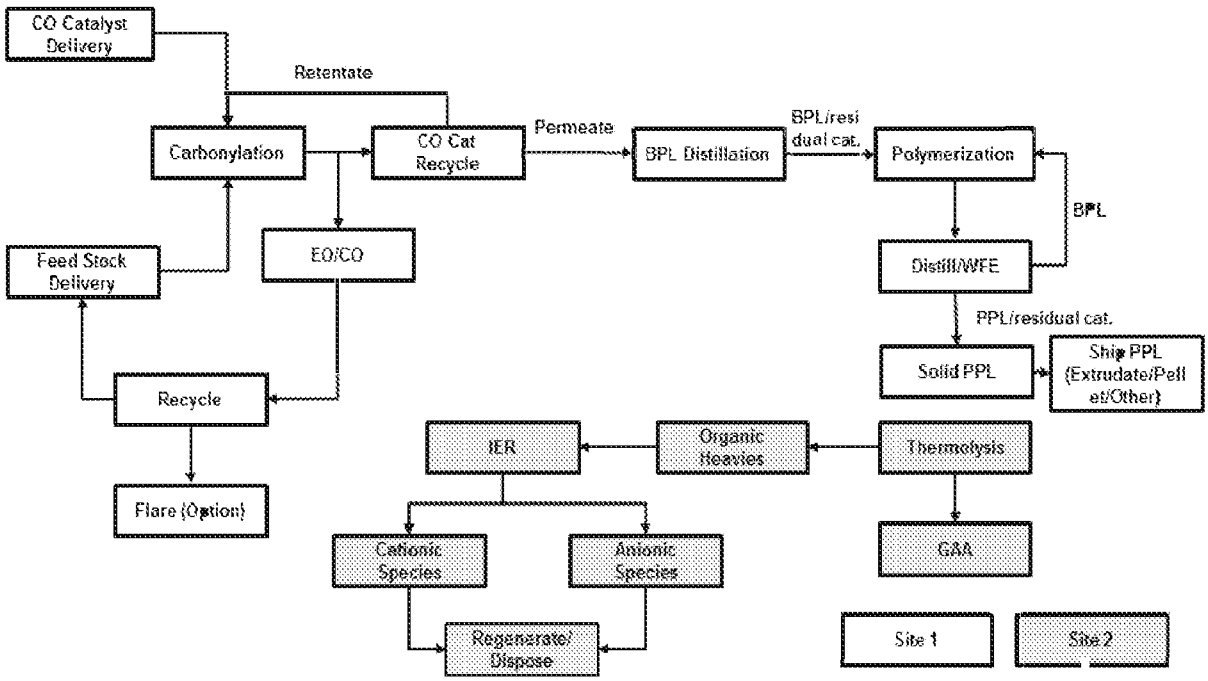

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose
Site 1
Site 2

FIG. 13

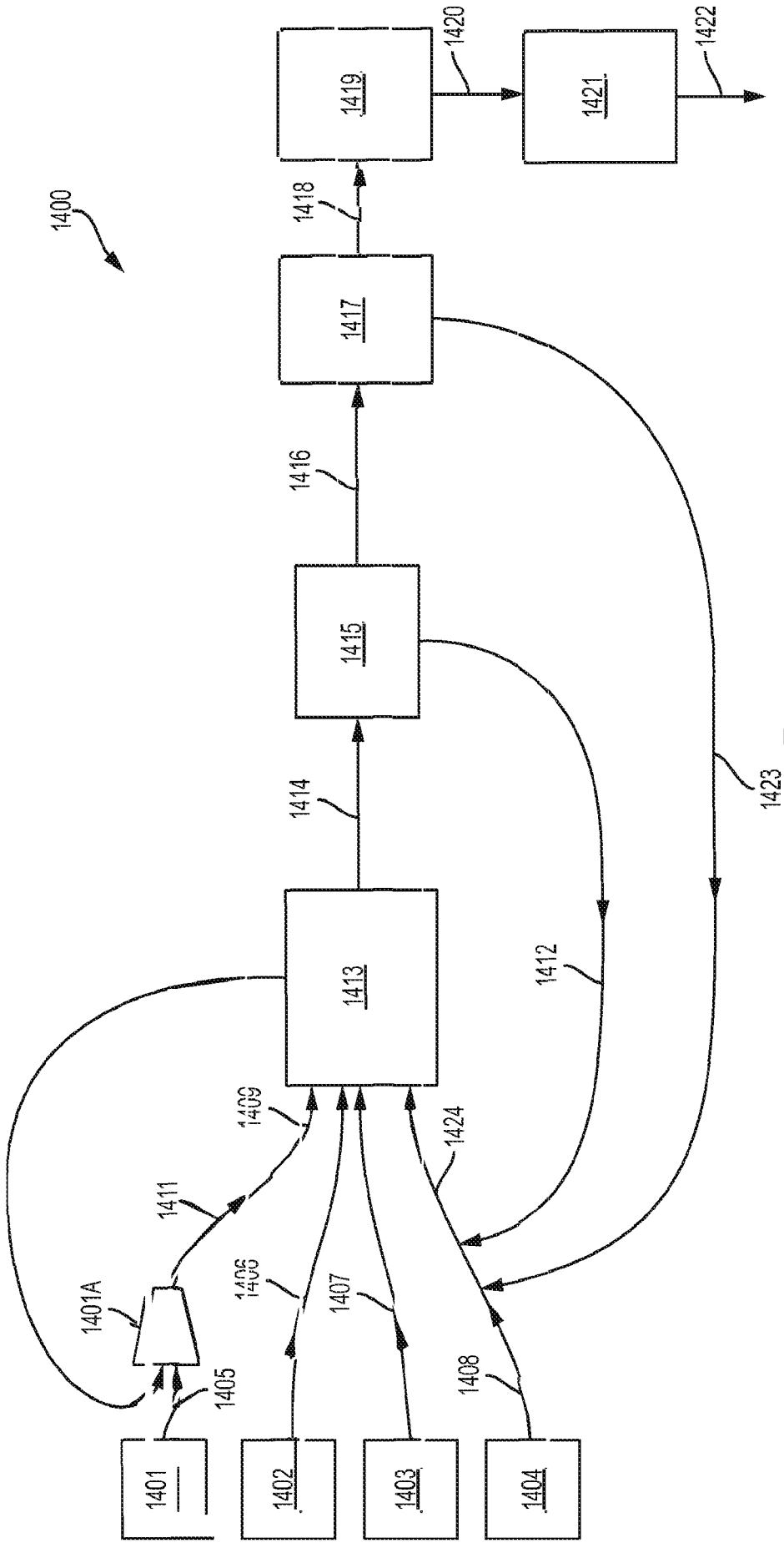

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FIG. 14

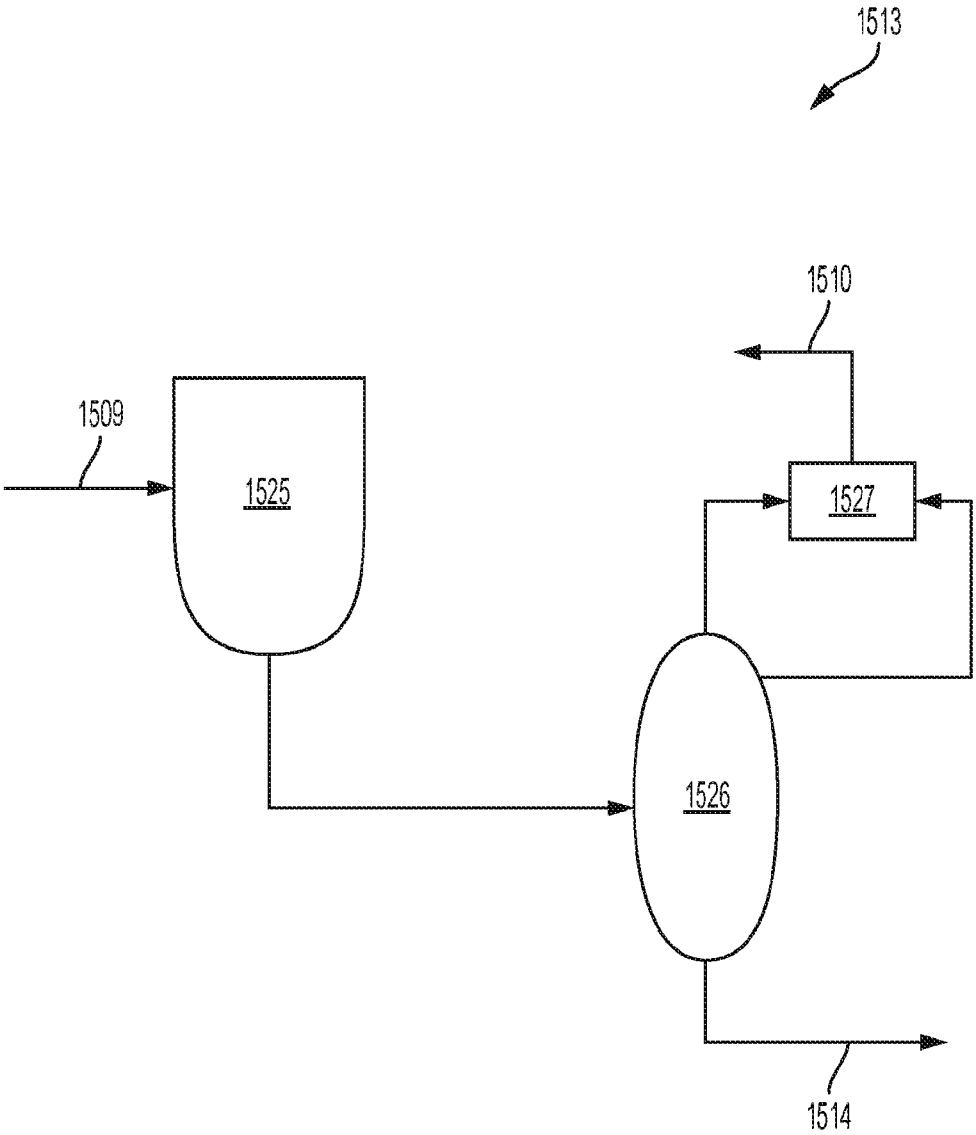


FIG.15

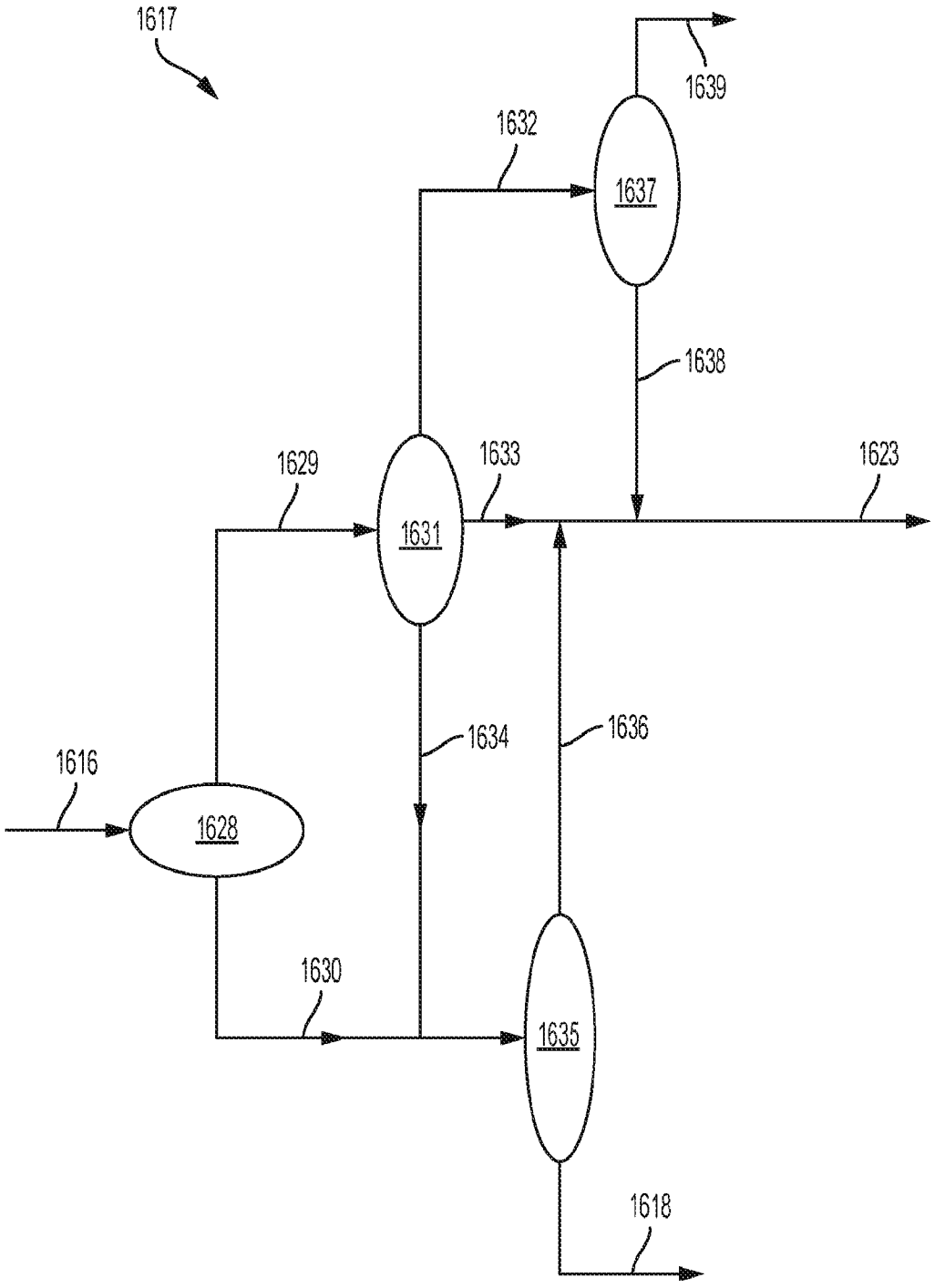

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FIG.16

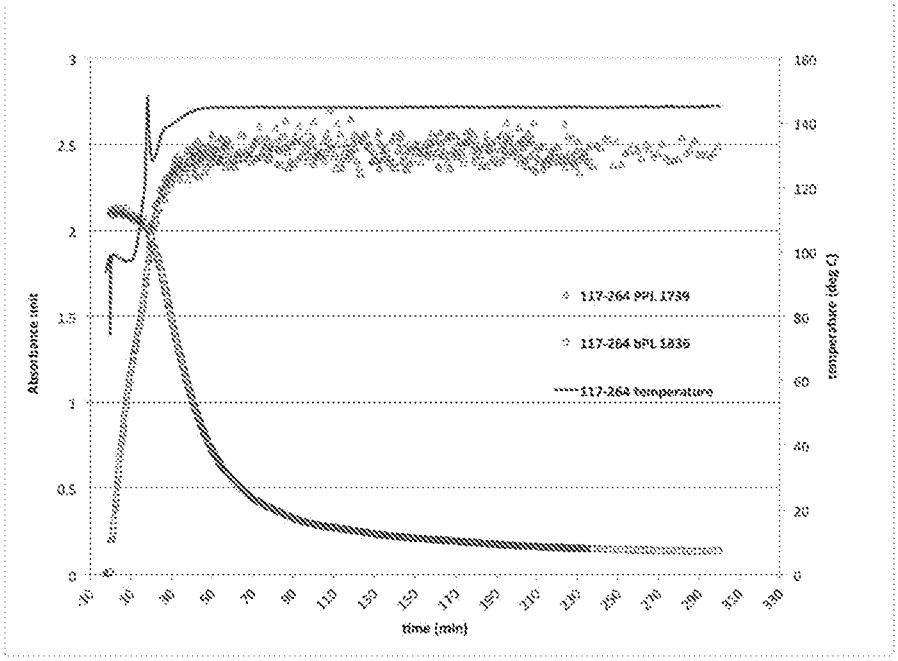

Absorbance unit
temperature (deg C)
time (min)
117-264 PPI 1736
117-264 BPI 1836
117-264 temperature

FIG. 17

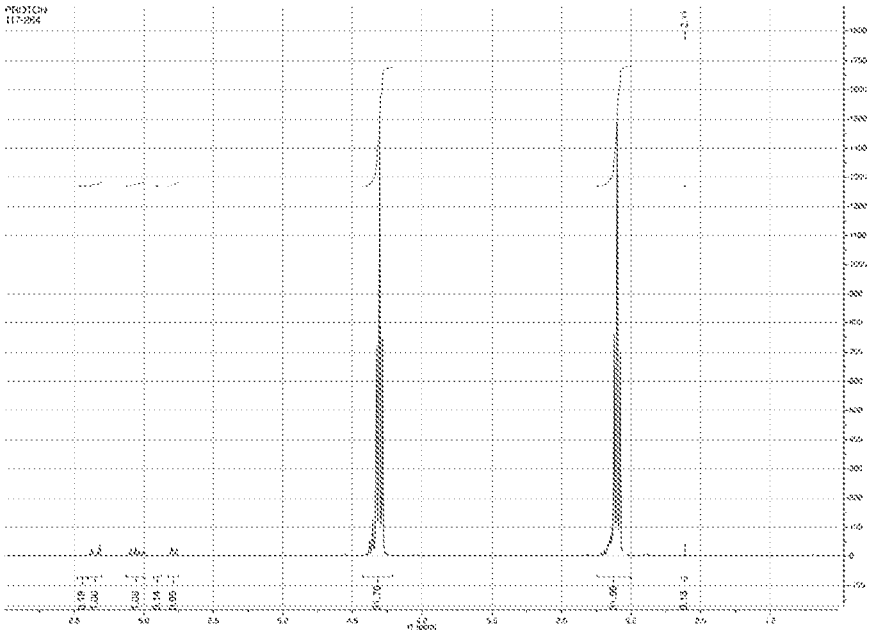


FIG. 18

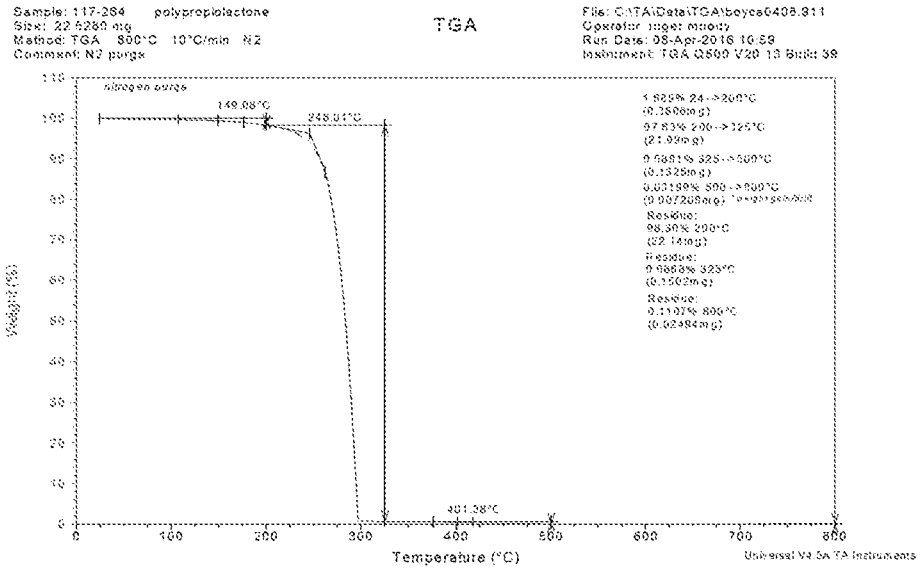

Sample: 117-264 polypropiolactone
Size: 22.5280 mg
Method: TGA 800°C 10°C/min N2
Comment: N2 purge
TGA
File: C:\TA\Data\TGA\boyce0408.911
Operator: inget mucoty
Run Date: 08-Apr-2016 10:58
Instrument: TGA Q500 V20.13 Build 39
Nitrogen purge
149.08°C
248.91°C
401.38°C
1.925% 24.-->200°C
(0.4360mg)
97.83% 200.-->325°C
(21.99mg)
0.5681% 325.-->500°C
(0.1325mg)
0.03198% 500.-->800°C
(0.007208mg)
Residue:
98.30% 200°C
(22.14mg)
Residue:
0.1868% 325°C
(0.1502mg)
Residue:
0.1101% 800°C
(0.02484mg)
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

FIG. 19

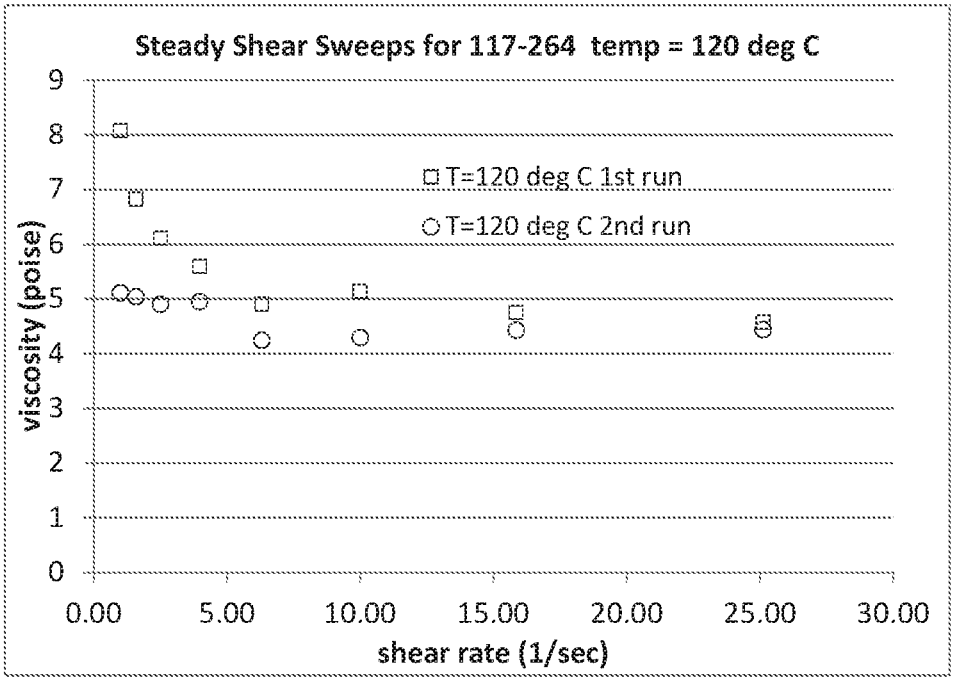

Steady Shear Sweeps for 117-264 temp = 120 deg C
T=120 deg C 1st run
T=120 deg C 2nd run
viscosity (poise)
shear rate (1/sec)
0
1
2
3
4
5
6
7
8
9
0.00
5.00
10.00
15.00
20.00
25.00
30.00

FIG. 20

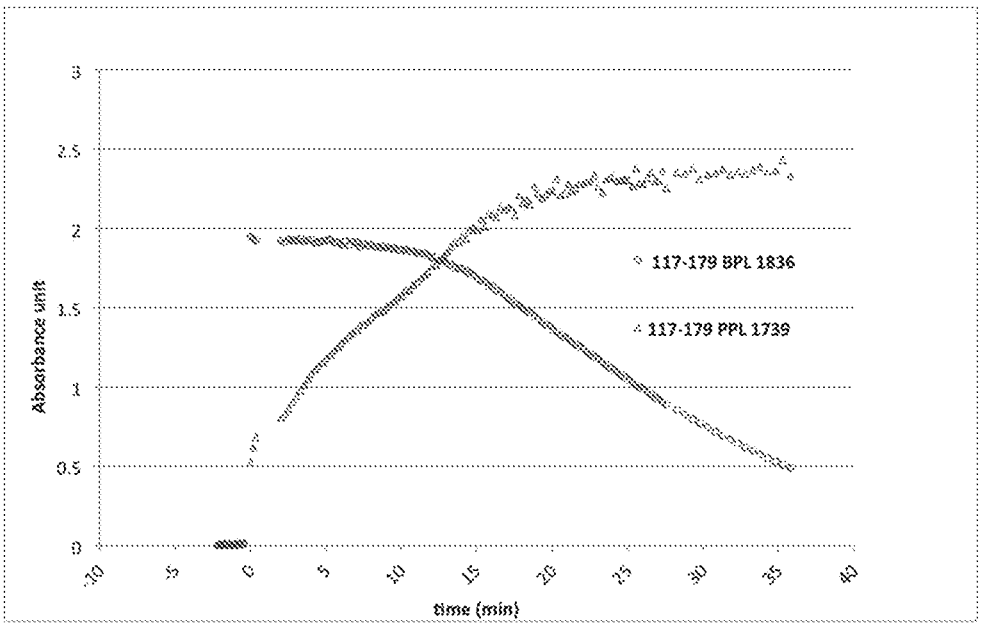


FIG. 21

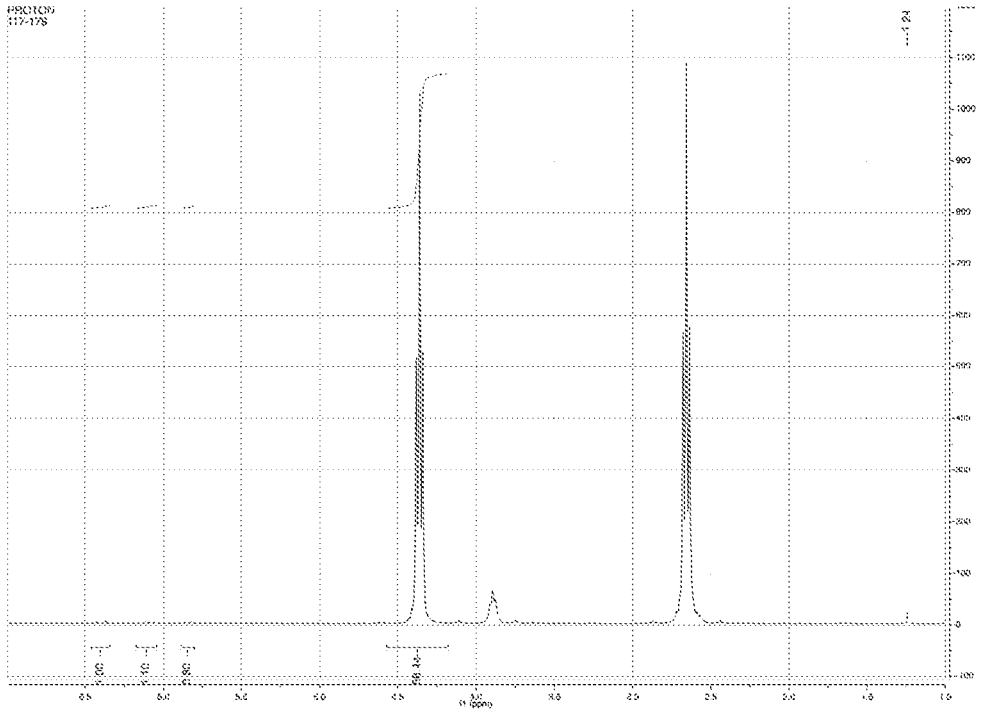


FIG. 22

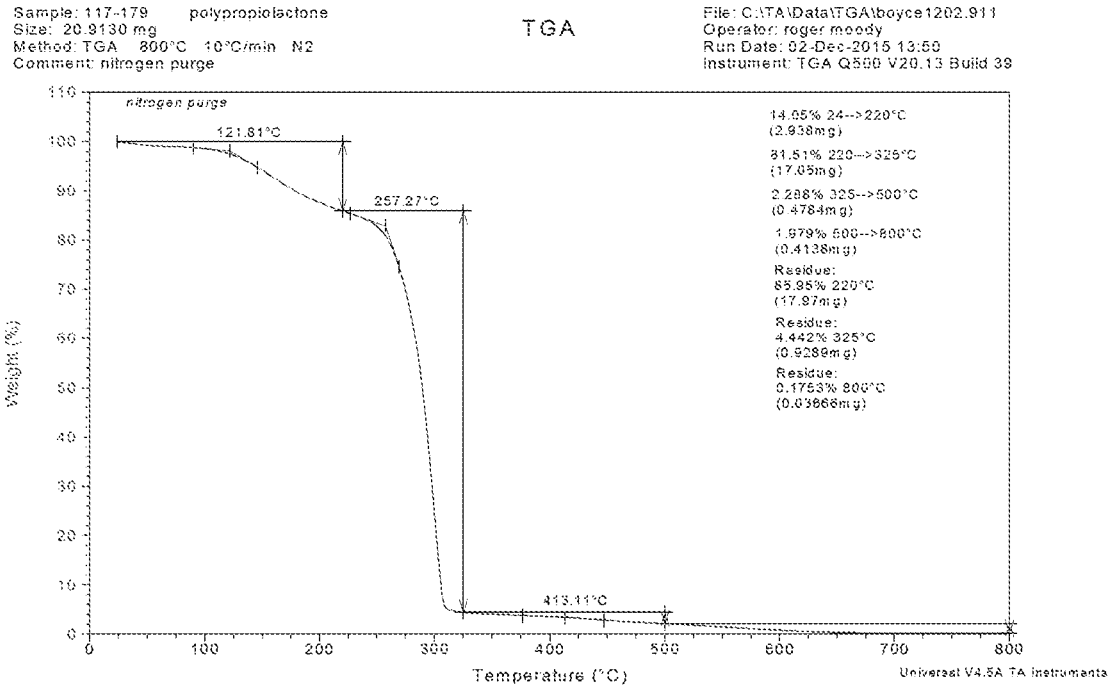

Sample: 117-179 polypropiolactone
Size: 20.9130 mg
Method: TGA 800°C 10°C/min N2
Comment: nitrogen purge
TGA
File: C:\TA\Data\TGA\boyce1202.911
Operator: roger moody
Run Date: 02-Dec-2015 13:50
Instrument: TGA Q500 V20.13 Build 39
nitrogen purge
121.81°C
257.27°C
413.11°C
14.05% 24-->220°C
(2.938mg)
81.51% 220-->325°C
(17.05mg)
2.288% 325-->500°C
(0.4784mg)
1.979% 500-->800°C
(0.4138mg)
Residue:
85.95% 220°C
(17.97mg)
Residue:
4.442% 325°C
(0.9289mg)
Residue:
0.1753% 800°C
(0.03666mg)
Weight (%)
Temperature (°C)
Universal V4.5A TA Instruments

FIG. 23

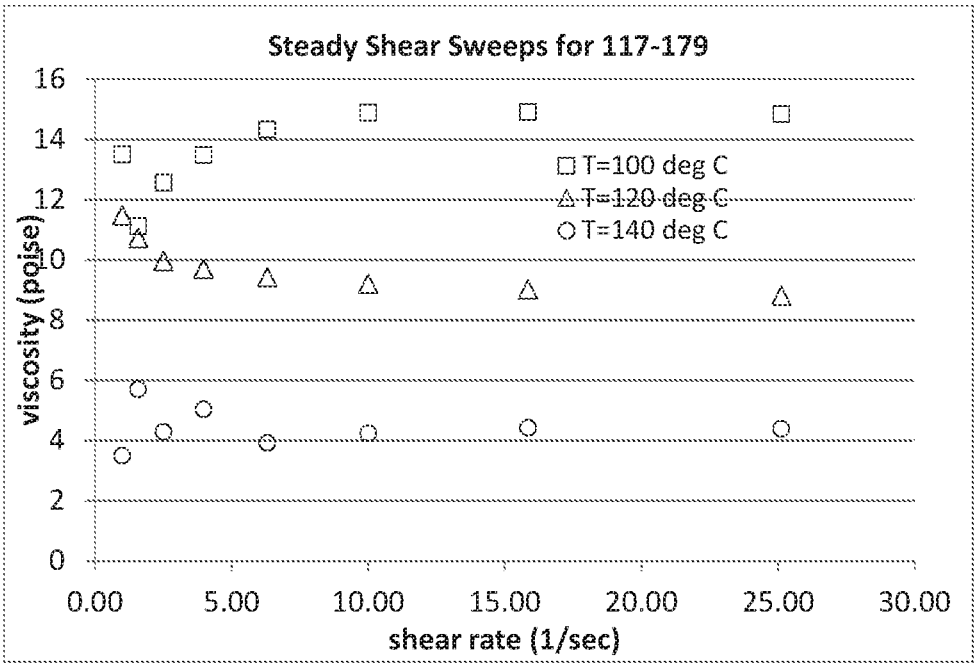

Steady Shear Sweeps for 117-179
T=100 deg C
T=120 deg C
T=140 deg C
viscosity (poise)
shear rate (1/sec)
0
2
4
6
8
10
12
14
16
0.00
5.00
10.00
15.00
20.00
25.00
30.00

FIG. 24

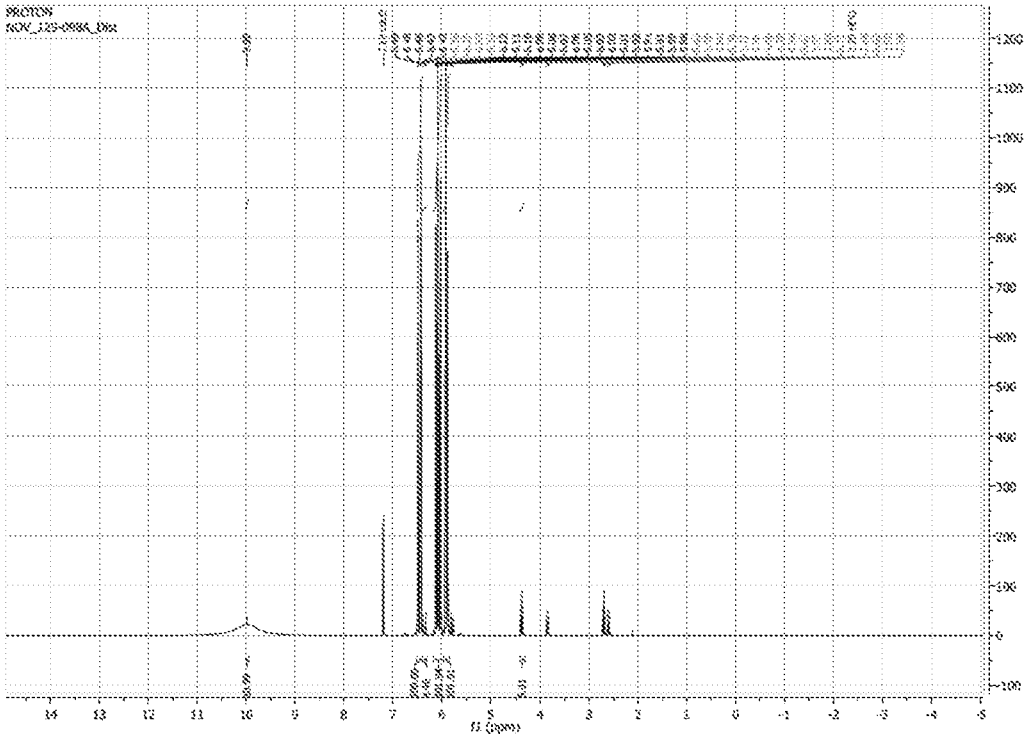


FIG. 25

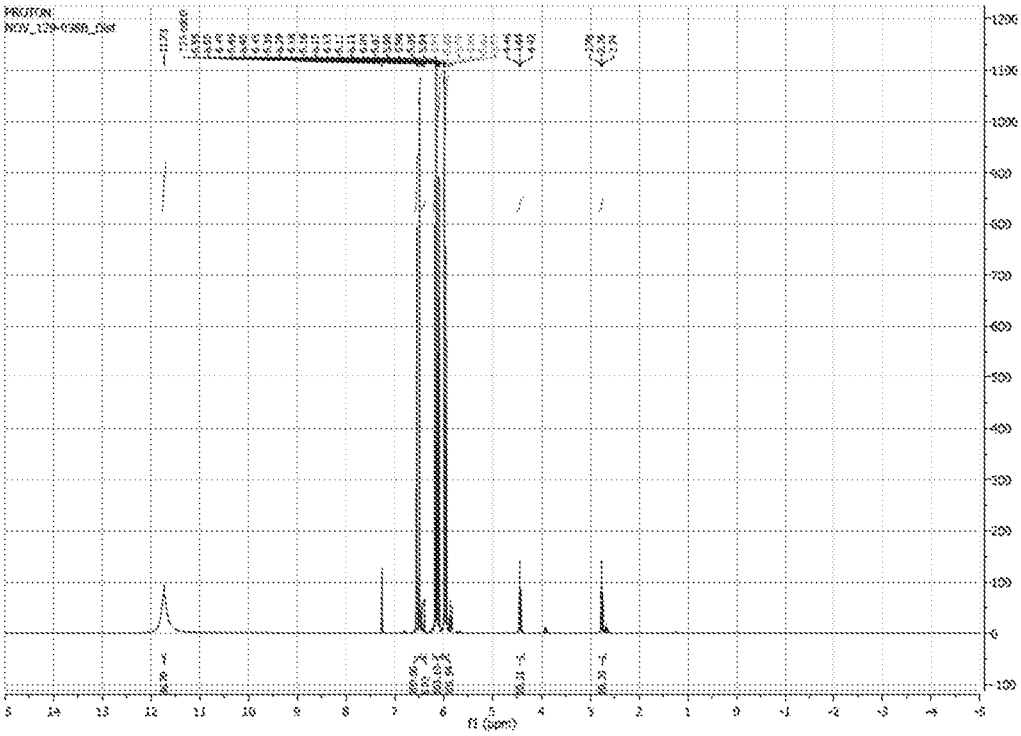


FIG. 26

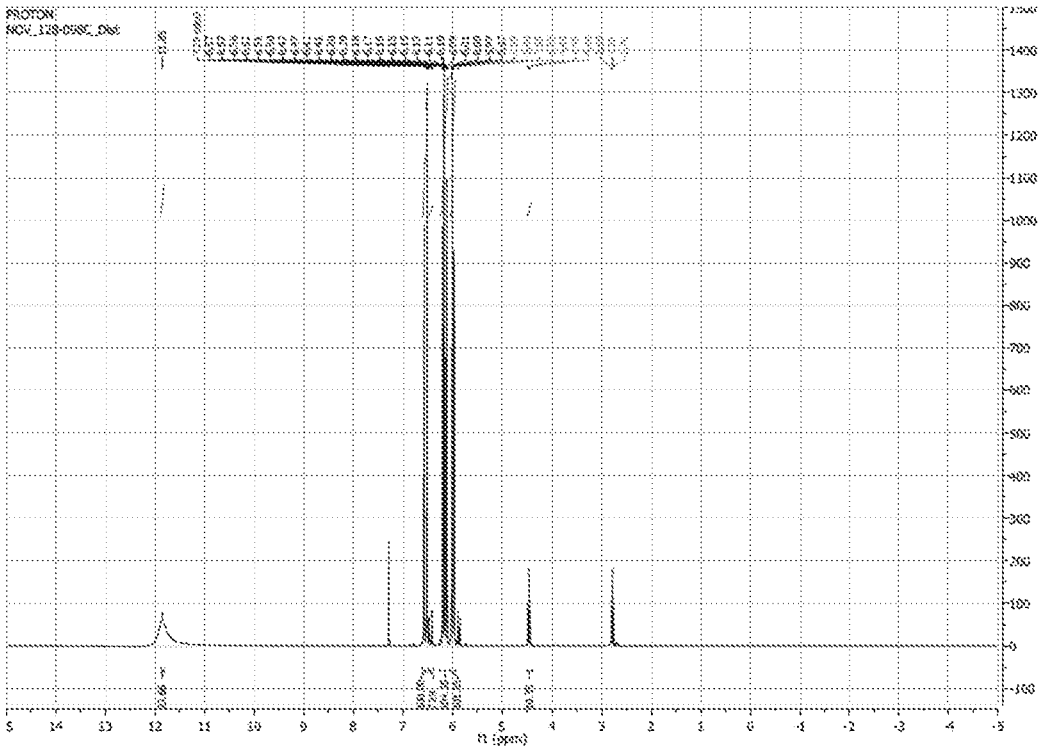


FIG. 27

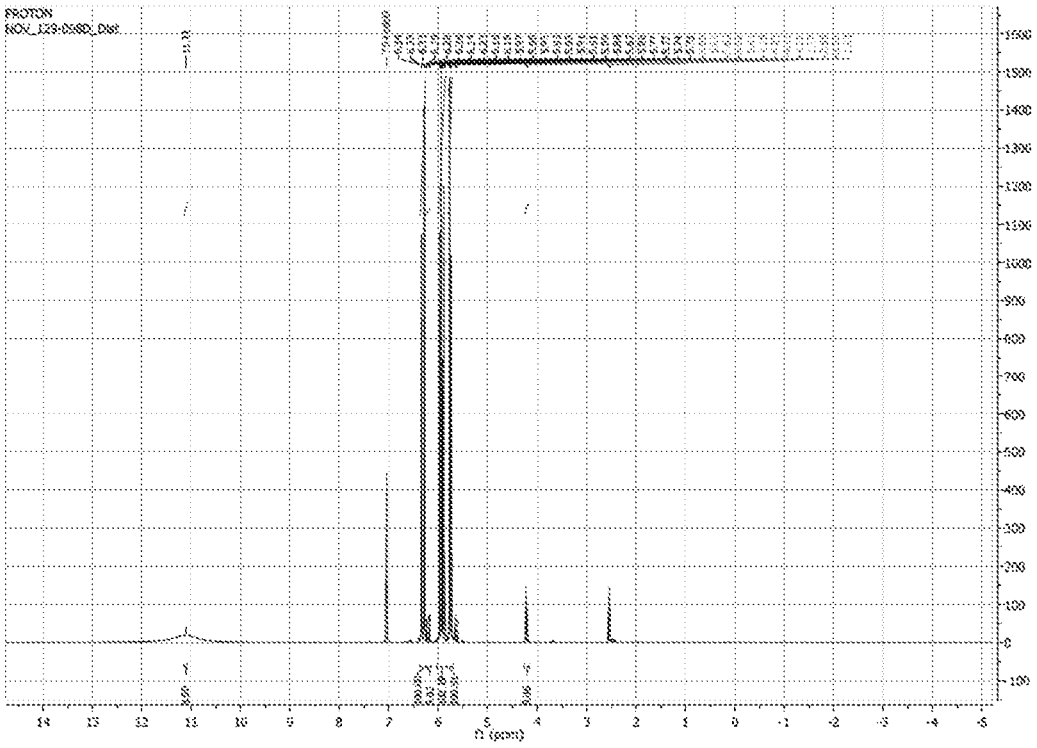


FIG. 28

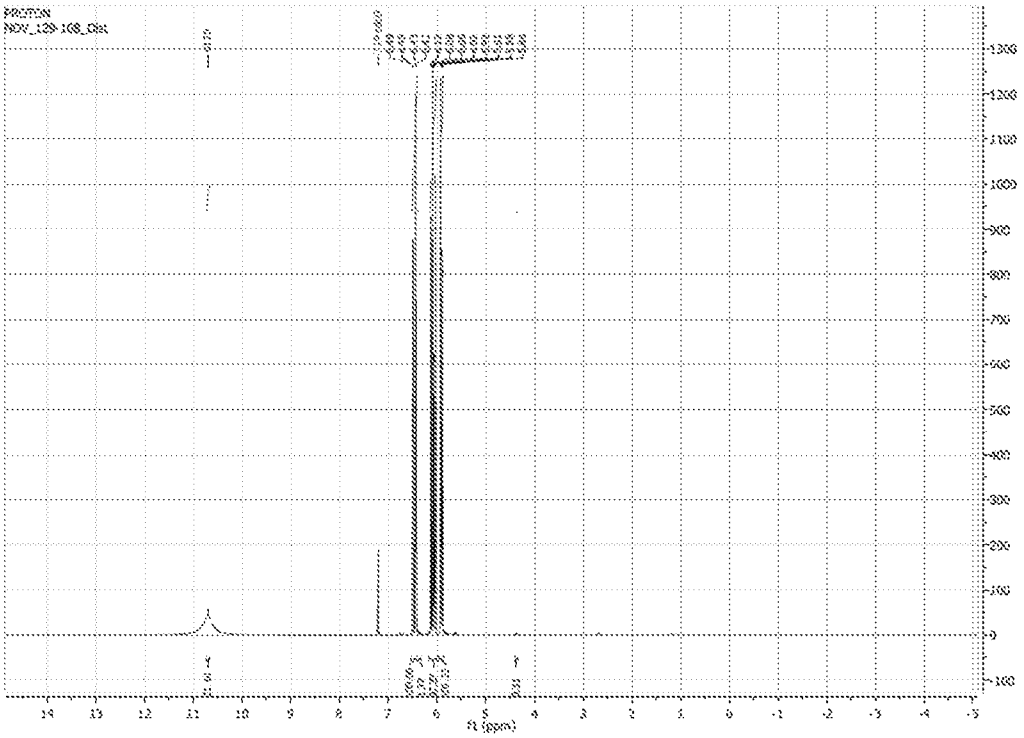


FIG. 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/044772

A. CLASSIFICATION OF SUBJECT MATTER

C07C 51/09(2006.01)i, C07C 51/12(2006.01)i, C07C 57/04(2006.01)i, C08G 63/08(2006.01)i, C08G 63/82(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C 51/09; C07D 305/12; C07C 67/27; C08G 63/82; C07C 67/30; C07C 57/04; C07C 51/12; C08G 63/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:acrylic acid, polypropiolactone, beta-propiolactone, ethylene oxide, carbon monoxide, carbonylation, polymerization, catalyst, thermolysis, recycle, purification

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013-126375 A1 (NOVOMER, INC.) 29 August 2013 See abstract; and pages 2, 4, 7-15.	27,28
Y		1-3
A		19,23-25,29
Y	WO 2013-185009 A1 (METABOLIX, INC.) 12 December 2013 See abstract; claim 59; and paragraphs [0061], [0072].	1-3
X	US 2014-0275575 A1 (NOVOMER, INC.) 18 September 2014 See abstract; and paragraphs [0003], [0004], [0014], [0049], [0050], [0072], [169], [0191], [0192].	29
Y		2
A	WO 2014-008232 A2 (NOVOMER, INC.) 09 January 2014 See abstract; and pages 2, 16, 17-19.	1-3,19,23-25,27-29
A	WO 2014-004858 A1 (NOVOMER, INC.) 03 January 2014 See the whole document.	1-3,19,23-25,27-29

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 November 2016 (08.11.2016)	**08 November 2016 (08.11.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
CHO, Han Sol
Telephone No. +82-42-481-5580

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/044772

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 6, 18
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 6 and 18 refer to an unsearchable claim which is not drafted in accordance with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4, 5, 7-17, 19(1), 20-22, 26
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/044772

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
L	International Application No. PCT/US2016/044927 filed on 29 July 2016 * Said application filed by the same applicant with the same priority (US 62/199,918 on 31 July 2015) comprises identical claims to those of this application. * Claim 19 found twice in this application and thus the second one was degignated as claim 19(1) by this Authority.	1-3,19,23-25,27-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/044772

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013-126375 A1	29/08/2013	AU 2013-222568 A1	11/09/2014
		CA 2864750 A1	29/08/2013
		CN 104245657 A	24/12/2014
		EP 2817285 A1	31/12/2014
		EP 2817285 A4	21/10/2015
		HK 1205499 A1	18/12/2015
		JP 2015-509497 A	30/03/2015
		KR 10-2014-0129182 A	06/11/2014
		SG 11201405138 A	27/11/2014
		US 2016-0016876 A1	21/01/2016
WO 2013-185009 A1	12/12/2013	CN 104350034 A	11/02/2015
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US 2014-0275575 A1	18/09/2014	CA 2757835 A1	14/10/2010
		CN 102421821 A	18/04/2012
		CN 102421821 B	10/12/2014
		CN 104529950 A	22/04/2015
		EP 2417182 A1	15/02/2012
		EP 2417182 A4	12/12/2012
		JP 2012-523421 A	04/10/2012
		JP 2015-108017 A	11/06/2015
		JP 5937001 B2	22/06/2016
		KR 10-2012-0023643 A	13/03/2012
		SG 175132 A1	28/11/2011
		US 2012-0123137 A1	17/05/2012
		US 2013-0281715 A1	24/10/2013
		US 2016-0102040 A1	14/04/2016
		US 8445703 B2	21/05/2013
		US 8796475 B2	05/08/2014
		US 9206144 B2	08/12/2015
		WO 2010-118128 A1	14/10/2010
WO 2014-008232 A2	09/01/2014	CA 2878028 A1	09/01/2014
		CN 104411661 A	11/03/2015
		EP 2867189 A2	06/05/2015
		EP 2867189 A4	16/03/2016
		JP 2015-523363 A	13/08/2015
		KR 10-2015-0027766 A	12/03/2015
		SG 11201408781 A	29/01/2015
		US 2015-0141693 A1	21/05/2015
		WO 2014-008232 A3	27/02/2014
WO 2014-004858 A1	03/01/2014	CA 2877903 A1	03/01/2014
		CN 104718236 A	17/06/2015
		EP 2867273 A1	06/05/2015
		EP 2867273 A4	24/02/2016
		JP 2015-522091 A	03/08/2015
		KR 10-2015-0036034 A	07/04/2015

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/044772

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		SG 11201408678 A	29/01/2015
		US 2015-0368394 A1	24/12/2015

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 February 2017 (09.02.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/023777 A9

(51) International Patent Classification:
C07C 51/09 (2006.01) *C08G 63/08* (2006.01)
C07C 51/12 (2006.01) *C08G 63/82* (2006.01)
C07C 57/04 (2006.01)

(21) International Application Number:
PCT/US2016/044772

(22) International Filing Date:
29 July 2016 (29.07.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/199,918 31 July 2015 (31.07.2015) US

(71) Applicant: **NOVOMER, INC.** [US/US]; 200 West St., Floor 4E, Waltham, Massachusetts 02451 (US).

(72) Inventors: **SOOKRAJ, Sadesh H.**; 200 West St., Floor 4E, Waltham, Massachusetts 02451 (US). **FARMER, Jay J.**; 1790 Ellis Hollow Rd., Ithaca, New York 14850 (US).

(74) Agent: **TOLOMEI, John**; 405 N. Wabash, Suite 2PE, Chicago, Illinois 60611 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(48) Date of publication of this corrected version:
12 October 2017

(15) Information about Correction:
see Notice of 12 October 2017

(54) Title: PRODUCTION SYSTEM/PRODUCTION PROCESS FOR ACRYLIC ACID AND PRECURSORS THEREOF

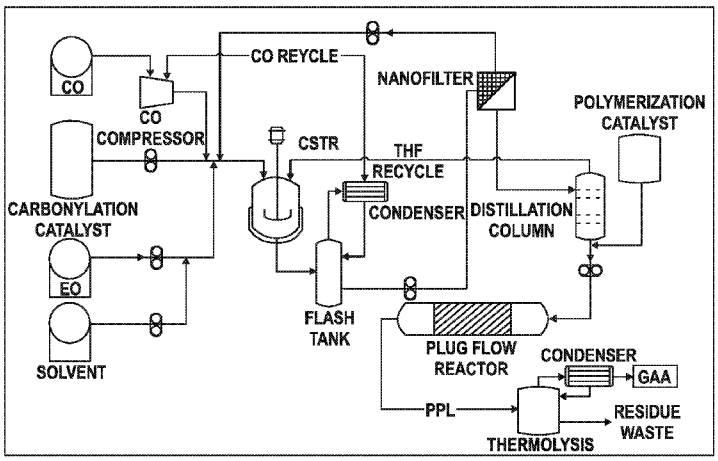


FIG. 1

(57) Abstract: Provided herein are systems, and methods of using such systems, for producing acrylic acid from ethylene oxide and carbon monoxide on an industrial scale. The production system/production processs has various unit operations, including, for example, a β-propiolactone production system/production process configured to produce β-propiolactone from ethylene oxide and carbon monoxide; a polypropiolactone production system/production process configured to produce polypropiolactone from ?-propiolactone; and a glacial acrylic acid production system/production process configured to produce acrylic acid with a high purity by thermolysis of polypropiolactone.

WO 2017/023777 A9

PRODUCTION SYSTEM/PRODUCTION PROCESS FOR ACRYLIC ACID AND PRECURSORS THEREOF

FIELD

[0001] The present disclosure relates generally to systems and methods for producing acrylic acid and precursors thereof, including β-propiolactone and polypropiolactone, from ethylene oxide and carbon monoxide.

BACKGROUND

[0002] Polypropiolactone is a biodegradable polymer that can be used in many packaging and thermoplastic applications. Polypropiolactone is also a useful precursor for the production of acrylic acid. Polypropiolactone may serve as a precursor for glacial acrylic acid, which is in high demand for the production of polyacrylic acid-based superabsorbent polymers, detergent co-builders, dispersants, flocculants and thickeners. One advantage of polypropiolactone is that it can be safely transported and stored for extended periods of time without the safety or quality concerns associated with shipping and storing glacial acrylic acid. There additionally is interest in glacial acrylic acid which can be produced from biomass-derived feedstock, petroleum-derived feedstock, or combinations thereof. Given the size of the acrylic acid market and the importance of downstream applications of acrylic acid, there is a need for industrial systems and methods to produce acrylic acid and precursors thereof.

BRIEF SUMMARY OF THE INVENTION

[0003] Provided herein are systems and processes for the production of acrylic acid and precursors thereof, including β-propiolactone and polypropiolactone, and methods of using such production system/production processs. In some aspects, provided is a production system/production process and a production process for glacial acrylic acid from ethylene oxide and carbon monoxide that includes a β-propiolactone production system/production process, a carbonylation catalyst recycling apparatus, a β-propiolactone purification system, a

polypropiolactone production system/production process, and a glacial acrylic acid production system/production process.

[0004] In some embodiments, the β-propiolactone production system/production process includes a carbon monoxide source, an ethylene oxide source, a carbonylation catalyst source, a solvent source, and a carbonylation reactor. In certain variations, the carbonylation reactor has at least one inlet to receive carbon monoxide from the carbon monoxide source, ethylene oxide from the ethylene oxide source, carbonylation catalyst from the carbonylation catalyst source, and solvent from the solvent source; and an outlet to output a first β-propiolactone stream, wherein the first β-propiolactone stream comprises β-propiolactone, solvent, ethylene oxide, carbonylation catalyst, acetaldehyde, and succinic anhydride.

[0005] In some embodiments, the carbonylation catalyst recycling apparatus is configured to separate at least a portion of the catalyst from the first β-propiolactone stream and produce a recycle catalyst stream and a second β-propiolactone stream. In some variations, the recycle catalyst stream includes separated carbonylation catalyst. In some variations, the second β-propiolactone stream includes β-propiolactone, solvent, ethylene oxide, catalyst, acetaldehyde, and succinic anhydride. In other embodiments, the carbonylation catalyst recycling apparatus has an inlet to receive the first β-propiolactone stream from the β-propiolactone production system/production process; a recycle outlet to output the recycle catalyst stream to the carbonylation reactor; and a β-propiolactone outlet to output the second β-propiolactone stream.

[0006] In other embodiments, the β-propiolactone purification system includes an evaporator, a stripper, and a vacuum column. In some variations, the evaporator is configured to receive the second β-propiolactone stream from the carbonylation catalyst recycling apparatus, and separate the second β-propiolactone stream into:

a first overhead stream that includes (i) at least 75 wt% of solvent, (ii) less than 20 wt% of β-propiolactone, and (iii) less than 5 wt% of ethylene oxide and acetaldehyde, and

a first bottoms stream that includes: (i) at least 75 wt% of β-propiolactone, (ii) less than 20 wt% of solvent, and (iii) less than 5 wt% of catalyst, acetaldehyde, and succinic anhydride.

[0007] In some variations, the stripper is configured to receive the first overhead stream from the evaporator, and separate the first overhead stream into:

a second overhead stream that includes (i) at least 25 wt% of ethylene oxide and acetaldehyde, and (ii) less than 75 wt% of solvent,

a side stream comprising solvent, and

a second bottoms stream comprising β-propiolactone.

[0008] In some variations, the vacuum column is configured to receive the first bottoms stream from the evaporator, and the second bottoms stream from the stripper and mix the first bottoms stream and the second bottoms stream to produce a mixed bottoms stream, separate the first bottoms stream and second bottoms stream into: a third overhead stream comprising solvent, and a third bottoms stream comprising β-propiolactone.

[0009] In some embodiments, the polypropiolactone production system/production process includes:

a polymerization initiator or catalyst source;

at least one polymerization reactor to receive the third bottoms stream from the β-propiolactone purification system and the polymerization initiator or catalyst from the polymerization initiator or catalyst source, and to output a polypropiolactone stream, wherein the polypropiolactone stream comprises polypropiolactone and β-propiolactone.

[0010] In other embodiments, the glacial acrylic acid production system/production process includes a thermolysis reactor, which has an inlet to receive the polypropiolactone stream from the polypropiolactone production system/production process, and an outlet to

output a glacial acrylic acid stream, wherein the glacial acrylic acid stream comprises glacial acrylic acid.

[0011] In other aspects, provided is a polypropiolactone production system/production process that includes: a β-propiolactone source; a polymerization initiator or catalyst source; a first polymerization reactor; and a second polymerization reactor.

[0012] In some variations, the first polymerization reactor includes: a β-propiolactone inlet to receive β-propiolactone from the β-propiolactone source; a first catalyst inlet to receive catalyst from the polymerization catalyst source; and a first mixture outlet to output a first mixture. In one variation, the first mixture comprises polypropiolactone, β-propiolactone, and polymerization catalyst.

[0013] In other variations, the second polymerization reactor positioned after the first polymerization reactor, and includes: a mixture inlet to receive the first mixture from the first polymerization reactor; a second catalyst inlet to receive additional polymerization catalyst from the carbonylation catalyst source; and a second mixture outlet to output a second mixture. In one variation, the second mixture comprises polypropiolactone, β-propiolactone, and polymerization catalyst.

[0014] In certain aspects, provided is a β-propiolactone polymerizer that includes: a mixing zone configured to mix β-propiolactone and a catalyst; and a plurality of cooling zones positioned after the mixing zone. In some variations, the β-propiolactone polymerizer has a reaction length. In certain variations, up to 95% of the β-propiolactone is polymerized in the presence of the initiator or catalyst to form polypropiolactone in the first 25% of the reaction length.

[0015] In other aspects, provided is a method for continuously producing polypropiolactone, that includes:

continuously feeding β-propiolactone into a first reactor;

continuously feeding catalyst into the first reactor;

producing a first mixture comprising polypropiolactone, unreacted β-propiolactone, and residual catalyst in the first reactor,

transferring the first mixture from the first reactor to a second reactor;

feeding additional catalyst from the catalyst source to the second reactor;

producing a second mixture comprising polypropiolactone, unreacted β-propiolactone, and residual catalyst in the second reactor.

[0016] In some variations of the method, the first reactor has: a β-propiolactone inlet to receive the β-propiolactone from a β-propiolactone source; a first catalyst inlet to receive the catalyst from a catalyst source; and a first mixture outlet to output the first mixture. In other variations of the method, the second reactor has: a mixture inlet to receive the first mixture from the first reactor; a second catalyst inlet to receive the additional catalyst from the catalyst source; and a second mixture outlet to output the second mixture.

[0017] In yet other aspects, provided is a polypropiolactone production system/production process that includes: a β-propiolactone source; a first reactor; and a second reactor. In some embodiments, the first reactor has: a β-propiolactone inlet to receive β-propiolactone from the β-propiolactone source, a bed of supported catalyst or supported catalyst precursor, and a first mixture outlet to output a first mixture. In one variation, the first mixture comprises polypropiolactone and unreacted β-propiolactone. In other embodiments, the second reactor is positioned after the first reactor. In some variations, the mixture inlet is configured to receive the first mixture from the first reactor, a second bed of supported catalyst or supported catalyst precursor, and a second mixture outlet to output a second mixture. In one variation, the second mixture comprises polypropiolactone and unreacted β-propiolactone.

[0018] In yet other aspects, provided is a solid transportable polymer composition that includes: at least 95 wt% of β-propiolactone; less than 10 ppm of cobalt or ions thereof; less

than 10 ppm of aluminum or ions thereof; less than 10 ppm acetic acid; and less than 10 ppm of tetrahydrofuran.

[0019] In another aspect, provided is a β-propiolactone purification system that includes: an evaporator; a first column, and a second column. In some embodiments, the evaporator configured to receive a feed stream, wherein the feed stream comprises β-propiolactone, solvent, and separate the feed stream into: a first overhead stream comprising: (i) at least 75 wt% solvent, and (ii) at most 20 wt% β-propiolactone; and a first bottoms stream comprising: (i) at least 75 wt% β-propiolactone, and (ii) at most 20 wt% solvent.

[0020] In some variations, the first column is configured to receive the first overhead stream from the evaporator, and separate the first overhead stream into: a second overhead stream comprising: (i) at least 35 wt% ethylene oxide, and (ii) at most 60 wt% solvent; a side stream comprising solvent; and a second bottoms stream comprising at least 75 wt% β-propiolactone.

[0021] In other variations, the second column is configured to receive the first bottoms stream from the evaporator, and the second bottoms stream from the first column, and separate the first bottoms stream and second bottoms stream into: a third overhead stream comprising at least 95 wt% solvent; and a third bottoms stream comprising at least 95 wt% β-propiolactone.

[0022] In one aspect, provided is a β-propiolactone composition that includes at least 95 wt% of β-propiolactone; less than 10 ppm of cobalt or ions thereof; less than 10 ppm of aluminum or ions thereof; less than 10 ppm acetic acid; and less than 10 ppm of tetrahydrofuran.

[0023] In yet other aspects, provided is a β-propiolactone production system/production process that includes: a carbon monoxide source; an ethylene oxide source; a carbonylation catalyst source; a solvent source; a recycled solvent storage tank; a reactor; and a purification apparatus. In some embodiments, the reactor has: at least one inlet to receive carbon monoxide

from the carbon monoxide source, ethylene oxide from the ethylene oxide source, carbonylation catalyst from the carbonylation catalyst source, and solvent from the solvent source and the recycled solvent storage tank; and an outlet to output a mixture, wherein the mixture comprises β-propiolactone, solvent, unreacted carbon monoxide, unreacted ethylene oxide, and carbonylation catalyst. In other embodiments, the purification apparatus is configured to: separate solvent from the mixture, and transfer the separated solvent to the recycled solvent reservoir.

[0024] In one aspect, provided is a glacial acrylic acid production system/production process that includes: a polypropiolactone source; and a reactor. In some embodiments, the polypropiolactone source includes: at least 95 wt% of polypropiolactone; less than 10 ppm of cobalt or ions thereof; less than 10 ppm of aluminum or ions thereof; less than 10 ppm acetic acid; and less than 10 ppm of tetrahydrofuran. In other embodiments, the reactor has: an inlet configured to receive the polypropiolactone from the polypropiolactone source; and an outlet configured to output a mixture, wherein the mixture comprises glacial acrylic acid.

[0025] In yet other aspects, provided is a separation system that includes: a feed source; a membrane; a first pump; and a second pump. In some embodiments, the membrane has: an inlet to receive a feed stream from the feed source, wherein the feed stream comprises β-propiolactone, catalyst and solvent; a catalyst outlet to output a catalyst recycling stream comprising catalyst and solvent; and a β-propiolactone outlet to output a β-propiolactone stream comprising β-propiolactone and solvent. In other embodiments, the first pump is configured to pump the feed stream from the feed source to the membrane. In yet other embodiments, the second pump is configured to pump the catalyst recycling stream to a β-propiolactone production system/production process.

DESCRIPTION OF THE FIGURES

[0026] The present application can be best understood by reference to the following description taken in conjunction with the accompanying figures, in which like parts may be referred to by like numerals.

[0027] FIG. **1** is a schematic illustration of a system to produce acrylic acid from carbon monoxide and ethylene oxide.

[0028] FIG. **2** is a schematic illustration of the unit operations to produce polypropiolactone from β-propiolactone, and glacial acrylic acid from polypropiolactone.

[0029] FIG. **3** is a schematic illustration of a carbonylation catalyst recycle system that employs membranes, configured to isolate residual carbonylation catalyst from a β-propiolactone product stream.

[0030] FIG. **4A** is a schematic illustration of a system for converting β-propiolactone to polypropiolactone that involves the use of two continuous stirred-tank reactors in series.

[0031] FIG. **4B** is a schematic illustration of a system for converting β-propiolactone to polypropiolactone that involves the use of two loop reactors in series.

[0032] FIG. **5** is a schematic illustration of a system for converting β-propiolactone to polypropiolactone that involves a plug flow reactor with multiple cooling zones.

[0033] FIGS. **6-13** depict various configurations of production system/production processs to produce glacial acrylic acid from ethylene oxide and carbon monoxide, via the production of β-propiolactone and polypropiolactone.

[0034] FIG. **14** illustrates an embodiment of an acrylic acid production system/production process described herein.

[0035] FIG. **15** illustrates an embodiment of a carbonylation reaction system described herein.

[0036] FIG. **16** illustrates an embodiment of a BPL purification system described herein.

[0037] FIGS. **17-20** are plots associated with Example 1 and show a plot of PPL and bPL peak absorbances as a function of time; an ^{1}H NMR of the isolated solid; a TGA of the isolated solid; and Melt rheology data of the isolated solid at 120°C.

[0038] FIGS. **21-24** are plots associated with Example 2 and show a plot of PPL and bPL peak absorbances as a function of time; an ^{1}H NMR of the isolated solid; a TGA of the isolated solid; and Melt rheology data of the isolated solid at 120°C.

[0039] FIGS. **25-28** are plots associated with Example 4 and show ^{1}H NMR plots indicating recovery of acrylic acid .

[0040] FIGS. **29** are plots associated with Example 5 and shows an ^{1}H NMR plot indicating recovery of acrylic acid.

DETAILED DESCRIPTION

[0041] The following description sets forth exemplary methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

Definitions

[0042] Definitions of specific functional groups and chemical terms are described in more detail below. The chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 75th Ed., inside cover, and specific functional groups are generally defined as described therein. Additionally, general principles of organic chemistry, as well as specific functional moieties and reactivity, are described in *Organic Chemistry*, Thomas Sorrell, University Science Books, Sausalito, 1999; Smith and March *March's Advanced Organic Chemistry*, 5th Edition, John Wiley & Sons, Inc., New York, 2001; Larock, *Comprehensive Organic Transformations*, VCH Publishers, Inc., New York, 1989; Carruthers, *Some Modern Methods of Organic Synthesis*, 3rd Edition,

Cambridge University Press, Cambridge, 1987; the entire contents of each of which are incorporated herein by reference.

[0043] The terms "halo" and "halogen" as used herein refer to an atom selected from fluorine (fluoro, –F), chlorine (chloro, –Cl), bromine (bromo, –Br), and iodine (iodo, –I).

[0044] The term "aliphatic" or "aliphatic group", as used herein, denotes a hydrocarbon moiety that may be straight–chain (i.e., unbranched), branched, or cyclic (including fused, bridging, and spiro–fused polycyclic) and may be completely saturated or may contain one or more units of unsaturation, but which is not aromatic. Unless otherwise specified, aliphatic groups contain 1–30 carbon atoms. In some embodiments, aliphatic groups contain 1–12 carbon atoms. In some embodiments, aliphatic groups contain 1–8 carbon atoms. In some embodiments, aliphatic groups contain 1–6 carbon atoms. In some embodiments, aliphatic groups contain 1–5 carbon atoms, in some embodiments, aliphatic groups contain 1–4 carbon atoms, in yet other embodiments aliphatic groups contain 1–3 carbon atoms, and in yet other embodiments, aliphatic groups contain 1–2 carbon atoms. Suitable aliphatic groups include, but are not limited to, linear or branched, alkyl, alkenyl, and alkynyl groups, and hybrids thereof such as (cycloalkyl)alkyl, (cycloalkenyl)alkyl or (cycloalkyl)alkenyl.

[0045] The term "heteroaliphatic," as used herein, refers to aliphatic groups wherein one or more carbon atoms are independently replaced by one or more atoms selected from the group consisting of oxygen, sulfur, nitrogen, phosphorus, or boron. In some embodiments, one or two carbon atoms are independently replaced by one or more of oxygen, sulfur, nitrogen, or phosphorus. Heteroaliphatic groups may be substituted or unsubstituted, branched or unbranched, cyclic or acyclic, and include "heterocycle," "heterocyclyl," "heterocycloaliphatic," or "heterocyclic" groups.

[0046] The term "acrylate" or "acrylates" as used herein refer to any acyl group having a vinyl group adjacent to the acyl carbonyl. The terms encompass mono-, di- and tri-substituted

vinyl groups. Examples of acrylates include, but are not limited to: acrylate, methacrylate, ethacrylate, cinnamate (3-phenylacrylate), crotonate, tiglate, and senecioate.

[0047] The term "polymer", as used herein, refers to a molecule of high relative molecular mass, the structure of which comprises the multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass. In some embodiments, a polymer is comprised of only one monomer species (e.g., polyethylene oxide). In some embodiments, a polymer is a copolymer, terpolymer, heteropolymer, block copolymer, or tapered heteropolymer of one or more epoxides.

[0048] The term "unsaturated", as used herein, means that a moiety has one or more double or triple bonds.

[0049] The terms "cycloaliphatic", "carbocycle", or "carbocyclic", used alone or as part of a larger moiety, refer to a saturated or partially unsaturated cyclic aliphatic monocyclic, bicyclic, or polycyclic ring systems, as described herein, having from 3 to 12 members, wherein the aliphatic ring system is optionally substituted as defined above and described herein. Cycloaliphatic groups include, without limitation, cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, cycloheptyl, cycloheptenyl, cyclooctyl, cyclooctenyl, and cyclooctadienyl. In some embodiments, the cycloalkyl has 3–6 carbons. The terms "cycloaliphatic", "carbocycle" or "carbocyclic" also include aliphatic rings that are fused to one or more aromatic or nonaromatic rings, such as decahydronaphthyl or tetrahydronaphthyl, where the radical or point of attachment is on the aliphatic ring. In some embodiments, a carbocyclic group is bicyclic. In some embodiments, a carbocyclic group is tricyclic. In some embodiments, a carbocyclic group is polycyclic.

[0050] The term "alkyl," as used herein, refers to saturated, straight– or branched–chain hydrocarbon radicals derived from an aliphatic moiety containing between one and six carbon atoms by removal of a single hydrogen atom. Unless otherwise specified, alkyl groups contain

1–12 carbon atoms. In some embodiments, alkyl groups contain 1–8 carbon atoms. In some embodiments, alkyl groups contain 1–6 carbon atoms. In some embodiments, alkyl groups contain 1–5 carbon atoms, in some embodiments, alkyl groups contain 1–4 carbon atoms, in yet other embodiments, alkyl groups contain 1–3 carbon atoms, and in yet other embodiments alkyl groups contain 1–2 carbon atoms. Examples of alkyl radicals include, but are not limited to, methyl, ethyl, n–propyl, isopropyl, n–butyl, iso–butyl, sec–butyl, sec–pentyl, iso–pentyl, tert–butyl, n–pentyl, neopentyl, n–hexyl, sec–hexyl, n–heptyl, n–octyl, n–decyl, n–undecyl, dodecyl, and the like.

[0051] The term "alkenyl," as used herein, denotes a monovalent group derived from a straight– or branched–chain aliphatic moiety having at least one carbon–carbon double bond by the removal of a single hydrogen atom. Unless otherwise specified, alkenyl groups contain 2–12 carbon atoms. In some embodiments, alkenyl groups contain 2–8 carbon atoms. In some embodiments, alkenyl groups contain 2–6 carbon atoms. In some embodiments, alkenyl groups contain 2–5 carbon atoms, in some embodiments, alkenyl groups contain 2–4 carbon atoms, in yet other embodiments, alkenyl groups contain 2–3 carbon atoms, and in yet other embodiments alkenyl groups contain 2 carbon atoms. Alkenyl groups include, for example, ethenyl, propenyl, butenyl, 1–methyl–2–buten–1–yl, and the like.

[0052] The term "alkynyl," as used herein, refers to a monovalent group derived from a straight– or branched–chain aliphatic moiety having at least one carbon–carbon triple bond by the removal of a single hydrogen atom. Unless otherwise specified, alkynyl groups contain 2–12 carbon atoms. In some embodiments, alkynyl groups contain 2–8 carbon atoms. In some embodiments, alkynyl groups contain 2–6 carbon atoms. In some embodiments, alkynyl groups contain 2–5 carbon atoms, in some embodiments, alkynyl groups contain 2–4 carbon atoms, in yet other embodiments alkynyl groups contain 2–3 carbon atoms, and in yet other

embodiments alkynyl groups contain 2 carbon atoms. Representative alkynyl groups include, but are not limited to, ethynyl, 2–propynyl (propargyl), 1–propynyl, and the like.

[0053] The term "carbocycle" and "carbocyclic ring" as used herein, refers to monocyclic and polycyclic moieties wherein the rings contain only carbon atoms. Unless otherwise specified, carbocycles may be saturated, partially unsaturated or aromatic, and contain 3 to 20 carbon atoms. Representative carbocyles include cyclopropane, cyclobutane, cyclopentane, cyclohexane, bicyclo[2,2,1]heptane, norbornene, phenyl, cyclohexene, naphthalene, and spiro[4.5]decane.

[0054] The term "aryl" used alone or as part of a larger moiety as in "aralkyl", "aralkoxy", or "aryloxyalkyl", refers to monocyclic and polycyclic ring systems having a total of five to 20 ring members, wherein at least one ring in the system is aromatic and wherein each ring in the system contains three to twelve ring members. The term "aryl" may be used interchangeably with the term "aryl ring". In some embodiments, "aryl" refers to an aromatic ring system which includes, but is not limited to, phenyl, naphthyl, anthracyl and the like, which may bear one or more substituents. Also included within the scope of the term "aryl", as it is used herein, is a group in which an aromatic ring is fused to one or more additional rings, such as benzofuranyl, indanyl, phthalimidyl, naphthimidyl, phenanthridinyl, or tetrahydronaphthyl, and the like.

[0055] The terms "heteroaryl" and "heteroar–", used alone or as part of a larger moiety, e.g., "heteroaralkyl", or "heteroaralkoxy", refer to groups having 5 to 14 ring atoms, preferably 5, 6, 9 or 10 ring atoms; having 6, 10, or 14 π electrons shared in a cyclic array; and having, in addition to carbon atoms, from one to five heteroatoms. The term "heteroatom" refers to nitrogen, oxygen, or sulfur, and includes any oxidized form of nitrogen or sulfur, and any quaternized form of a basic nitrogen. Heteroaryl groups include, without limitation, thienyl, furanyl, pyrrolyl, imidazolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, isothiazolyl, thiadiazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, indolizinyl,

purinyl, naphthyridinyl, benzofuranyl and pteridinyl. The terms "heteroaryl" and "heteroar–", as used herein, also include groups in which a heteroaromatic ring is fused to one or more aryl, cycloaliphatic, or heterocyclyl rings, where the radical or point of attachment is on the heteroaromatic ring. Non-limiting examples include indolyl, isoindolyl, benzothienyl, benzofuranyl, dibenzofuranyl, indazolyl, benzimidazolyl, benzthiazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, 4*H*–quinolizinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, phenoxazinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, and pyrido[2,3–b]–1,4–oxazin–3(4H)–one. A heteroaryl group may be monocyclic or bicyclic. The term "heteroaryl" may be used interchangeably with the terms "heteroaryl ring", "heteroaryl group", or "heteroaromatic", any of which terms include rings that are optionally substituted. The term "heteroaralkyl" refers to an alkyl group substituted by a heteroaryl, wherein the alkyl and heteroaryl portions independently are optionally substituted.

[0056] As used herein, the terms "heterocycle", "heterocyclyl", "heterocyclic radical", and "heterocyclic ring" are used interchangeably and refer to a stable 5– to 7–membered monocyclic or 7- to 14-membered bicyclic heterocyclic moiety that is either saturated or partially unsaturated, and having, in addition to carbon atoms, one or more, preferably one to four, heteroatoms, as defined above. When used in reference to a ring atom of a heterocycle, the term "nitrogen" includes a substituted nitrogen. As an example, in a saturated or partially unsaturated ring having 0–3 heteroatoms selected from oxygen, sulfur or nitrogen, the nitrogen may be N (as in 3,4–dihydro–2*H*–pyrrolyl), NH (as in pyrrolidinyl), or $^{+}$NR (as in *N*–substituted pyrrolidinyl).

[0057] A heterocyclic ring can be attached to its pendant group at any heteroatom or carbon atom that results in a stable structure and any of the ring atoms can be optionally substituted. Examples of such saturated or partially unsaturated heterocyclic radicals include, without limitation, tetrahydrofuranyl, tetrahydrothienyl, pyrrolidinyl, pyrrolidonyl, piperidinyl,

pyrrolinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, decahydroquinolinyl, oxazolidinyl, piperazinyl, dioxanyl, dioxolanyl, diazepinyl, oxazepinyl, thiazepinyl, morpholinyl, and quinuclidinyl. The terms "heterocycle", "heterocyclyl", "heterocyclyl ring", "heterocyclic group", "heterocyclic moiety", and "heterocyclic radical", are used interchangeably herein, and also include groups in which a heterocyclyl ring is fused to one or more aryl, heteroaryl, or cycloaliphatic rings, such as indolinyl, 3*H*–indolyl, chromanyl, phenanthridinyl, or tetrahydroquinolinyl, where the radical or point of attachment is on the heterocyclyl ring. A heterocyclyl group may be mono– or bicyclic. The term "heterocyclylalkyl" refers to an alkyl group substituted by a heterocyclyl, wherein the alkyl and heterocyclyl portions independently are optionally substituted.

[0058] As used herein, the term "partially unsaturated" refers to a ring moiety that includes at least one double or triple bond. The term "partially unsaturated" is intended to encompass rings having multiple sites of unsaturation, but is not intended to include aryl or heteroaryl moieties, as herein defined.

[0059] As described herein, compounds may contain "optionally substituted" moieties. In general, the term "substituted", whether preceded by the term "optionally" or not, means that one or more hydrogens of the designated moiety are replaced with a suitable substituent. Unless otherwise indicated, an "optionally substituted" group may have a suitable substituent at each substitutable position of the group, and when more than one position in any given structure may be substituted with more than one substituent selected from a specified group, the substituent may be either the same or different at every position. Combinations of substituents envisioned may include those that result in the formation of stable or chemically feasible compounds. The term "stable", as used herein, refers to compounds that are not substantially altered when subjected to conditions to allow for their production, detection, and,

in some embodiments, their recovery, purification, and use for one or more of the purposes disclosed herein.

[0060] In some chemical structures herein, substituents are shown attached to a bond which crosses a bond in a ring of the depicted molecule. This means that one or more of the substituents may be attached to the ring at any available position (usually in place of a hydrogen atom of the parent structure). In cases where an atom of a ring so substituted has two substitutable positions, two groups may be present on the same ring atom. When more than one substituent is present, each is defined independently of the others, and each may have a different structure. In cases where the substituent shown crossing a bond of the ring is –R, this has the same meaning as if the ring were said to be "optionally substituted" as described in the preceding paragraph.

[0061] Suitable monovalent substituents on a substitutable carbon atom of an "optionally substituted" group are independently halogen; $-(CH_2)_{0-4}R^\circ$; $-(CH_2)_{0-4}OR^\circ$; $-O-(CH_2)_{0-4}C(O)OR^\circ$; $-(CH_2)_{0-4}CH(OR^\circ)_2$; $-(CH_2)_{0-4}SR^\circ$; $-(CH_2)_{0-4}Ph$, which may be substituted with R°; $-(CH_2)_{0-4}O(CH_2)_{0-1}Ph$ which may be substituted with R°; –CH=CHPh, which may be substituted with R°; $-NO_2$; –CN; $-N_3$; $-(CH_2)_{0-4}N(R^\circ)_2$; $-(CH_2)_{0-4}N(R^\circ)C(O)R^\circ$; $-N(R^\circ)C(S)R^\circ$; $-(CH_2)_{0-4}N(R^\circ)C(O)NR^\circ_2$; $-N(R^\circ)C(S)NR^\circ_2$; $-(CH_2)_{0-4}N(R^\circ)C(O)OR^\circ$; $-N(R^\circ)N(R^\circ)C(O)R^\circ$; $-N(R^\circ)N(R^\circ)C(O)NR^\circ_2$; $-N(R^\circ)N(R^\circ)C(O)OR^\circ$; $-(CH_2)_{0-4}C(O)R^\circ$; $-C(S)R^\circ$; $-(CH_2)_{0-4}C(O)OR^\circ$; $-(CH_2)_{0-4}C(O)N(R^\circ)_2$; $-(CH_2)_{0-4}C(O)SR^\circ$; $-(CH_2)_{0-4}C(O)OSiR^\circ_3$; $-(CH_2)_{0-4}OC(O)R^\circ$; $-OC(O)(CH_2)_{0-4}SR^\circ$, $-SC(S)SR^\circ$; $-(CH_2)_{0-4}SC(O)R^\circ$; $-(CH_2)_{0-4}C(O)NR^\circ_2$; $-C(S)NR^\circ_2$; $-C(S)SR^\circ$; $-SC(S)SR^\circ$, $-(CH_2)_{0-4}OC(O)NR^\circ_2$; $-C(O)N(OR^\circ)R^\circ$; $-C(O)C(O)R^\circ$; $-C(O)CH_2C(O)R^\circ$; $-C(NOR^\circ)R^\circ$; $-(CH_2)_{0-4}SSR^\circ$; $-(CH_2)_{0-4}S(O)_2R^\circ$; $-(CH_2)_{0-4}S(O)_2OR^\circ$; $-(CH_2)_{0-4}OS(O)_2R^\circ$; $-S(O)_2NR^\circ_2$; $-(CH_2)_{0-4}S(O)R^\circ$; $-N(R^\circ)S(O)_2NR^\circ_2$; $-N(R^\circ)S(O)_2R^\circ$; $-N(OR^\circ)R^\circ$; $-C(NH)NR^\circ_2$; $-P(O)_2R^\circ$; $-P(O)R^\circ_2$; $-OP(O)R^\circ_2$; $-OP(O)(OR^\circ)_2$; SiR°_3; $-(C_{1-4}$ straight or branched alkylene$)O-N(R^\circ)_2$; or $-(C_{1-4}$

straight or branched alkylene)C(O)O–N(R°)$_2$, wherein each R° may be substituted as defined below and is independently hydrogen, C$_{1-8}$ aliphatic, –CH$_2$Ph, –O(CH$_2$)$_{0-1}$Ph, or a 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur, or, notwithstanding the definition above, two independent occurrences of R°, taken together with their intervening atom(s), form a 3–12–membered saturated, partially unsaturated, or aryl mono– or polycyclic ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur, which may be substituted as defined below.

[0062] Suitable monovalent substituents on R° (or the ring formed by taking two independent occurrences of R° together with their intervening atoms), are independently halogen, –(CH$_2$)$_{0-2}$R$^\bullet$, –(haloR$^\bullet$), –(CH$_2$)$_{0-2}$OH, –(CH$_2$)$_{0-2}$OR$^\bullet$, –(CH$_2$)$_{0-2}$CH(OR$^\bullet$)$_2$; -O(haloR$^\bullet$), –CN, –N$_3$, –(CH$_2$)$_{0-2}$C(O)R$^\bullet$, –(CH$_2$)$_{0-2}$C(O)OH, –(CH$_2$)$_{0-2}$C(O)OR$^\bullet$, -(CH$_2$)$_{0-4}$C(O)N(R°)$_2$; –(CH$_2$)$_{0-2}$SR$^\bullet$, –(CH$_2$)$_{0-2}$SH, –(CH$_2$)$_{0-2}$NH$_2$, –(CH$_2$)$_{0-2}$NHR$^\bullet$, -(CH$_2$)$_{0-2}$NR$^\bullet_2$, –NO$_2$, –SiR$^\bullet_3$, –OSiR$^\bullet_3$, –C(O)SR$^\bullet$, –(C$_{1-4}$ straight or branched alkylene)C(O)OR$^\bullet$, or –SSR$^\bullet$ wherein each R$^\bullet$ is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently selected from C$_{1-4}$ aliphatic, -CH$_2$Ph, –O(CH$_2$)$_{0-1}$Ph, or a 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur. Suitable divalent substituents on a saturated carbon atom of R° include =O and =S.

[0063] Suitable divalent substituents on a saturated carbon atom of an "optionally substituted" group include the following: =O, =S, =NNR*$_2$, =NNHC(O)R*, =NNHC(O)OR*, =NNHS(O)$_2$R*, =NR*, =NOR*, –O(C(R*$_2$))$_{2-3}$O–, or –S(C(R*$_2$))$_{2-3}$S–, wherein each independent occurrence of R* is selected from hydrogen, C$_{1-6}$ aliphatic which may be substituted as defined below, or an unsubstituted 5–6–membered saturated, partially unsaturated, or aryl ring having 0-4 heteroatoms independently selected from nitrogen, oxygen,

and sulfur. Suitable divalent substituents that are bound to vicinal substitutable carbons of an "optionally substituted" group include: $-O(CR^*_2)_{2-3}O-$, wherein each independent occurrence of R^* is selected from hydrogen, C_{1-6} aliphatic which may be substituted as defined below, or an unsubstituted 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0064] Suitable substituents on the aliphatic group of R^* include halogen, $-R^\bullet$, -(halo$R^\bullet$), –OH, $-OR^\bullet$, -O(halo$R^\bullet$), –CN, –C(O)OH, $-C(O)OR^\bullet$, $-NH_2$, $-NHR^\bullet$, $-NR^\bullet_2$, or $-NO_2$, wherein each $R^\bullet$ is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently C_{1-4} aliphatic, $-CH_2Ph$, $-O(CH_2)_{0-1}Ph$, or a 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0065] Suitable substituents on a substitutable nitrogen of an "optionally substituted" group include $-R^\dagger$, $-NR^\dagger_2$, $-C(O)R^\dagger$, $-C(O)OR^\dagger$, $-C(O)C(O)R^\dagger$, $-C(O)CH_2C(O)R^\dagger$, $-S(O)_2R^\dagger$, $-S(O)_2NR^\dagger_2$, $-C(S)NR^\dagger_2$, $-C(NH)NR^\dagger_2$, or $-N(R^\dagger)S(O)_2R^\dagger$; wherein each $R^\dagger$ is independently hydrogen, C_{1-6} aliphatic which may be substituted as defined below, unsubstituted –OPh, or an unsubstituted 5–6–membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur, or, notwithstanding the definition above, two independent occurrences of $R^\dagger$, taken together with their intervening atom(s) form an unsubstituted 3–12–membered saturated, partially unsaturated, or aryl mono– or bicyclic ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0066] Suitable substituents on the aliphatic group of $R^\dagger$ are independently halogen, $-R^\bullet$, –(halo$R^\bullet$), –OH, $-OR^\bullet$, -O(halo$R^\bullet$), –CN, –C(O)OH, $-C(O)OR^\bullet$, $-NH_2$, $-NHR^\bullet$, $-NR^\bullet_2$, or $-NO_2$, wherein each $R^\bullet$ is unsubstituted or where preceded by "halo" is substituted only with one or more halogens, and is independently C_{1-4} aliphatic, $-CH_2Ph$, $-O(CH_2)_{0-1}Ph$, or a

5-6-membered saturated, partially unsaturated, or aryl ring having 0–4 heteroatoms independently selected from nitrogen, oxygen, and sulfur.

[0067] As used herein, the term "catalyst" refers to a substance the presence of which increases the rate of a chemical reaction, while not being consumed or undergoing a permanent chemical change itself.

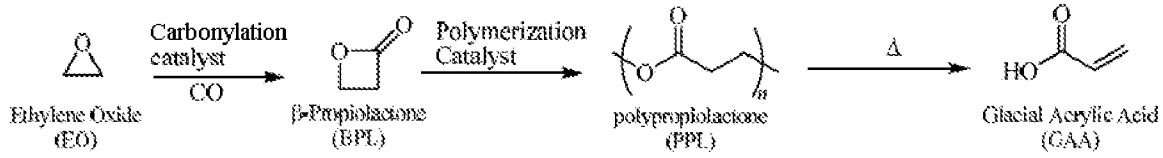
[0068] As used herein, the term "about" preceding one or more numerical values means the numerical value ±5%. It should be understood that reference to "about" a value or parameter herein includes (and describes) embodiments that are directed to that value or parameter per se. For example, description referring to "about x" includes description of "x" per se.

[0069] Further, it should be understood that reference to "between" two values or parameters herein includes (and describes) embodiments that include those two values or parameters per se. For example, description referring to "between x and y" includes description of "x" and "y" per se.

[0070] The mass fractions disclosed herein can be converted to wt% by multiplying by 100.

Glacial Acrylic Acid Production system/production process

[0071] Glacial acrylic acid can be produced from ethylene oxide and carbon monoxide according to the following general reaction scheme:



Ethylene oxide ("EO") may undergo a carbonylation reaction, *e.g.*, with carbon monoxide ("CO"), in the present of a carbonylation catalyst to produce β-propiolactone ("bPL"). The β-propiolactone may undergo polymerization in the presence of a polymerization catalyst to

produce polypropiolactone ("PPL"). The polypropiolactone may undergo thermolysis to produce glacial acrylic acid ("GAA").

[0072] PPL may undergo thermolysis by one of two primary reaction mechanisms as disclosed by (Iwabuchi, S., Jaacks, V., Galil, F. and Kern, W. (1973), The thermal degradation of poly(oxycarbonylethylene) (poly-β-propiolactone). Makromol. Chem., 165: 59–72). The desired mechanism is referred to as unzipping and it converts a PPL polymer with a chain length of "n" into one molecule of acrylic acid and reduces the PPL polymer chain length to n-1. The other method is referred to as chain scission; chain scission converts a PPL polymer of chain length n into a PPL polymer of chain length of less than n-2 and a PPL polymer of chain length of at least 2.

[0073] Product acrylic acid is susceptible to auto-polymerization via two mechanisms, either Michael addition or radical polymerization. Michael addition forms a product of two molecules of acrylic acid which is a di-acrylic acid ester and identical to a PPL of chain length 2. There is no known inhibitor of Michael addition of acrylic acid, but under thermolysis conditions this reaction is reversible and can decompose back into two molecules of acrylic acid. The product of Radical polymerization of acrylic acid produces polyacrylic acid, and will not normally convert back into acrylic acid under thermolysis conditions. There are many known inhibitors for radical polymerization of acrylic acid, including but not limited to phenothiazine (PTZ) and 4-methoxyphenol (MEHQ). Under many circumstances, a stream of radical polymerization inhibitor (either neat or in appropriate solvent) is added in batch or continuous mode to the primary thermolysis reactor or mixed with PPL stream before introduction to reactor to combat losses of acrylic acid to polyacrylic acid in thermolysis reactor.

[0074] Thermolysis of PPL may be catalyzed by the presence of a depolymerization catalyst. Depolymerization catalyst (either neat or in appropriate solvent) may be added in

batch or continuous mode to the primary thermolysis reactor or mixed with PPL stream before introduction to reactor to reduce severity of thermolysis reaction conditions (which reduces conversion of acrylic acid to polyacrylic acid). Optimally, the catalyst employed for bPL polymerization can be used as a depolymerization catalyst as well. The thermolysis reactor can be designed (see below) such that the concentrations of the polymerization catalyst species in the PPL inlet stream and in the thermolysis reactor, which along with the difference in reactor conditions and stream compositions accounts for the seemingly divergent functions.

[0075] Provided herein are systems and methods for the production of glacial acrylic acid from ethylene oxide and carbon monoxide on an industrial scale. For example, in some aspects, the systems and methods described herein are suitable for the production of glacial acrylic acid on a scale of 25 kilo tons per annum ("KTA"). In some variations, the systems provided herein are configured to produce glacial acrylic acid in a continuous process, and further feedback loops to continually produce acrylic acid.

[0076] Further, in some variations, the systems provided herein further include various purification systems to produce glacial acrylic acid of high purity. For example, the systems provided herein may be configured to remove residual carbonylation catalyst, carbonylation solvent, and by-products (*e.g.*, acetaldehyde, succinic anhydride, and acrylic acid dimer) to achieve glacial acrylic acid with a purity of at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%.

[0077] In other variations, the systems provided herein are also configured to recycle various starting materials and glacial acrylic acid precursors, such as poly-propiolactone. For example, the systems may include one or more recycle systems to isolate unreacted ethylene oxide, unreacted carbon monoxide, carbonylation solvent, and catalyst.

[0078] In yet other variations, the systems provided herein are also configured to manage and integrate heat produced. The carbonylation reaction to produce β-propiolactone and the

polymerization reaction to produce polypropiolactone are exothermic. Thus, the heat generated from the exothermic unit operations, such as the carbonylation reactor and polymerization reactor can be captured and used for cooling in endothermic unit operations, such as the distillation apparatus and thermolysis reactor. For example, in some variations of the systems and methods provided herein, steam may be generated in heat transfer equipment (*e.g.*, shell and tube heat exchanger and reactor cooling jacket) via a temperature gradient between process fluid and water/steam. This steam can be used for heat integration between exothermic and endothermic unit operations. In other variations of the systems and methods provided herein, other suitable heat transfer fluids may be used.

[0079] In other variations, heat integration may be achieved by combining certain unit operations. For example, heat integration may be achieved by combining polymerization of β-propiolactone and vaporization of the solvent (*e.g.*, THF) from the distillation column within a single unit operation. In such a configuration, the heat liberated from the β-propiolactone polymerization reaction is used directly to vaporize the solvent in the distillation apparatus, and the output of the unit produces polypropiolactone. In other variations, the heat liberated from the polymerization reaction can be exported to other systems at the same production site.

[0080] With reference to FIG. **1**, an exemplary system to produce acrylic acid from carbon monoxide and ethylene oxide is depicted. Carbon monoxide (CO), a carbonylation catalyst, ethylene oxide (EO) and carbonylation solvent are fed into a β-propiolactone production system/production process, depicted as a continuous stirred tank reactor (CSTR) in FIG. **1**. Such β-propiolactone production system/production process is typically configured to produce a liquid product stream of β-propiolactone. This β-propiolactone product stream is fed to an EO/CO separator, depicted as the flash tank in FIG. **1**, where unreacted ethylene oxide and unreacted carbon monoxide may be separated and recycled for use in the CSTR. The β-propiolactone product stream is then fed from the EO/CO separator to a carbonylation catalyst

recycle system, depicted as a nanofilter in FIG. **1**. The carbonylation catalyst recycle system is configured to separate residual carbonylation catalyst present in the β-propiolactone product stream, and such separated carbonylation catalyst may be recycled for use in the CSTR. The nanofilter depicted in FIG. **1** may be any suitable membrane, such as a polymeric membrane or a ceramic membrane, and produces a retentate stream typically made up of β-propiolactone, carbonylation solvent, residual carbonylation catalyst, small amounts of ethylene oxide, carbon monoxide, and by-products (such as acetaldehyde and succinic anhydride), and a permeate stream typically made up of β-propiolactone, carbonylation solvent, small amounts of ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and succinic anhydride) and trace amounts of carbonylation catalyst. In some embodiments, trace amount is less than 1% by wt, less than 0.5% by wt, less than 0.01% by wt, less than 0.005% by wt, less than 0.001% by wt, or less than 0.0001% by wt. In certain embodiments, trace amount is below the detection threshold of the measurement method being used.

[0081] The permeate is fed into a β-propiolactone purification system, depicted as a distillation column in FIG. **1**, which is configured to separate ethylene oxide, carbon monoxide, and by-products from the solvent recycle stream, which is depicted as a tetrahydrofuran (THF) recycle stream. The system in FIG. **1** depicts the use of THF as the carbonylation solvent, but it should be understood that in other variations, other suitable solvents may be used. The purified β-propiolactone stream from the β-propiolactone purification system and polymerization catalyst are fed into a polypropiolactone production system/production process, depicted as a plug flow reactor in FIG. **1**. The polypropiolactone production system/production process is configured to produce a polypropiolactone product stream, which can be fed into a thermolysis reactor to produce glacial acrylic acid.

[0082] It should be understood, however, that while FIG. **1** depicts an exemplary glacial acrylic acid production system/production process, variations of this productions system are

envisioned. For example, while a CSTR is depicted as the reactor in the β-propiolactone production system/production process, other reactors and reactor configurations may be employed. In another example, while a distillation column and a plug flow reactor are depicted in FIG. **1** in the β-propiolactone purification system and polypropiolactone productions system, respectively, other separation apparatuses and other reactors and reactor configurations may be employed.

[0083] Additionally, in other exemplary embodiments of the systems described herein, various unit operations depicted in FIG. **1** may be combined or omitted. In some variations, the β-propiolactone production system/production process and membrane unit operations may be combined (e.g. membrane reactor) or polymerization and depolymerization may be combined (e.g. catalytic or reactive distillation) may be combined, or the EO/CO separator may be omitted.

[0084] Further, it should be understood that in other exemplary embodiments of systems described herein, additional unit operations may be employed. For example, in some embodiments it may be possible to incorporate one or more ion exchange resins into the systems to remove various cationic and anionic catalyst species that may result from the use of the carbonylation catalyst. In other embodiments, one or more heat exchangers may be incorporated into the systems to manage and integrate heat produced in the system.

[0085] In yet other embodiments the process and/or system by which it is practiced may employ a variety of sensors and control equipment to automate control of the process and any related system. For example, the various reactors, in particular a β-propiolactone reactor, used in the process and any related system may employ a sensor to detect amounts of water and oxygen in the reactor or that enters the reactor. Such sensor may be connected to a control that can adjust parameters to maintain water and oxygen content under a predefined amount. Such sensor may monitor the carbonylation catalyst to detect amounts of water and oxygen in the

reactor and may be connected to a control that can control the amount of carbonylation catalyst from the carbonylation catalyst source. In addition, or alternatively the carbon monoxide source may comprise a sensor configured to detect amounts of water and oxygen in the reactor and such sensor may be connected to a control that can control the amount of carbon monoxide from the carbon monoxide source. In addition, or alternatively the ethylene oxide source may comprises a sensor configured to detect amounts of water and oxygen in the reactor and such sensor may be connected to a control that can control the amount of ethylene oxide from the ethylene oxide source.

[0086] Provided herein are various systems configured for the commercial production of polypropiolactone (PPL) and glacial acrylic acid (GAA). In some configurations, PPL and GAA are produced at the same geographical location. In other configurations, PPL is produced in one location and shipped to a second location where GAA is produced.

[0087] In other variations of such configurations, the residual carbonylation catalyst (which may include cationic and anionic species) may be removed at various points in the production system/production process. For example, in certain configurations, the residual carbonylation catalyst may be removed from the PPL product stream prior to thermolysis to produce GAA. In other configurations, the residual carbonylation catalyst may be removed, if desired to do so, after thermolysis by distillation or other separation means.

[0088] In yet other variations, β-propiolactone (bPL) may be polymerized to produce PPL by way of complete conversion of bPL. In such a variation, there may not be a need for additional apparatus in the system to isolate and recycle bPL to the polymerization reactor. In other variations, the conversion of bPL is not complete. Unreacted bPL may be separated from the PPL product stream and the recovered bPL may be recycled back to the polymerization reactor.

[0089] These variations in the configurations of the systems are described in further detail with respect to FIGS. **6-13**. FIG. **6** depicts an exemplary system wherein the PPL product stream and the GAA product stream are produced at the same location, at least a portion of the carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, and the polypropiolactone production system/production process is configured to achieve complete conversion of bPL to PPL.

[0090] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0091] The BPL production system/production process (labeled 'Carbonylation' in FIG. **6**) typically includes a carbon monoxide (CO) source, an ethylene oxide (EO) source, a carbonylation catalyst source, a solvent source, and a carbonylation reactor. In certain variations, the carbonylation reactor is configured to receive carbon monoxide (CO), ethylene oxide (EO), and solvent from a CO source, an EO source, and a solvent source (collectively labeled 'Feed Stock Delivery' in FIG. **6**). The carbonylation reactor is further configured to receive a carbonylation catalyst from a carbonylation catalyst source (labeled 'CO Catalyst Delivery' in FIG. **6**). The carbon monoxide, ethylene oxide, carbonylation solvent, and carbonylation catalyst may be obtained by any commercially available sources, or any commercially available methods and techniques known in the art.

[0092] In some variations, the CO, EO, and solvent are essentially water and oxygen free. In one variation, the solvent from the solvent source, the EO from the EO source, and the CO

from the CO source have a concentration of water and oxygen less than about 500 ppm, less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, less than about 10 ppm, less than about 2 ppm, or less than 1 ppm.

[0093] Any suitable carbonylation solvents may be used. In some embodiments, the carbonylation solvent comprises tetrahydrofuran, hexane, or a combination thereof. In other embodiments, the carbonylation solvent comprises an ether, a hydrocarbon, or a combination thereof. In yet other embodiments, the carbonylation solvent comprises tetrahydrofuran, tetrahydropyran, 2,5-dimethyl tetrahydrofuran, sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, propyl acetate, butyl acetate, 2-butanone, cyclohexanone, toluene, difluorobenzene, dimethoxy ethane, acetone, or methylethyl ketone, or any combination thereof. In one variation, the carbonylation solvent comprises tetrahydrofuran.

[0094] The carbonylation catalyst used herein may be made on-site and/or off-site. In some embodiments, the carbonylation catalyst is a cobalt-aluminum catalyst. In certain embodiments, the carbonylation catalyst comprises a carbonyl cobaltate in combination with an aluminum porphyrin compound, a carbonyl cobaltate in combination with an aluminum salen compound, or a carbonyl cobaltate in combination with an aluminum salophen compound. In one variation, the carbonylation catalyst is $(Al(TPP)Co(CO)_4)$.

[0095] The carbonylation reactor may be a continuous reactor, such as a continuous stirred tank reactor (CSTR). Other reactors described herein, such as batch reactors, plug flow reactors (PFR), and semi-batch reactors may also be employed.

[0096] With reference again to the exemplary system in FIG. **6**, the carbonylation reactor may be configured to receive EO from the EO source at any rate, temperature, or pressure

described herein. For example, in some embodiments, the inlet to the carbonylation reactor receives EO from an EO source at about 1000 kg/hr to 25000 kg/hr. In some embodiments, the inlet to the carbonylation reactor receives EO from an EO source at about 30 kmol/hr to about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reactor is configured to receive EO from an EO source at a temperature between about 10°C to about 30°C. In some embodiments, the inlet to the carbonylation reactor is configured to receive EO from an EO source at a pressure between about 20 bar to about 100 bar and in a more narrow range 50 bar to 70 bar.

[0097] With reference again to the exemplary system in FIG. **6**, the carbonylation reactor may be configured to receive CO from the CO source at any rate, temperature, or pressure described herein. For example, in some embodiments, the inlet to the carbonylation reactor is configured to receive CO from a CO source at a temperature between about 10°C to about 170°C and more narrowly between 10°C to about 70°C. In some embodiments, the inlet to the carbonylation reactor is configured to receive CO from a CO source at a pressure between about 20 bar to about 100 bar and more narrowly 50 and 70 bar. In some embodiments, the CO source that supplies CO to the carbonylation reactor is a fresh carbon monoxide source (i.e., main CO feed), or recycled carbon monoxide from the β-propiolactone production system/production process, or a combination thereof. In some embodiments, the fresh CO source is configured to provide between about 1000 kg/hr CO to about 16000 kg/hr CO. In some embodiments, the fresh CO source is configured to provide between about 30 kmol/hr CO to about 600 kmol/hr CO. In some embodiments, the recycled CO from the β-propiolactone production system/production process can provide between about 100 kg/hr CO to about 3500 kg/hr CO. In some embodiments, the recycled CO source is configured to provide between about 3 kmol/hr CO to about 150 kmol/hr CO.

[0098] With reference again to the exemplary system in FIG. **6**, the carbonylation reactor may be configured to receive solvent at any rate, temperature, or pressure described herein. For example, in some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at a rate of between about 10000 kg/hr to about 130000 kg/hr. In some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at rate of between about 150 kmol/hr to about 1900 kmol/hr. In some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at a temperature between about 10°C to about 160°C and more narrowly 10°C to about 60°C. In some embodiments, the inlet to the carbonylation reactor is configured to receive solvent from a solvent feed at a pressure of between about 20 bar to about 100 bar and more narrowly 50 bar to 65 bar. In some embodiments, the solvent feed that supplies solvent to the carbonylation reactor can include solvent from a fresh solvent source, recycled solvent from the BPL purification system (e.g., BPL distillation system), and/or solvent in the recycled carbonylation catalyst stream from the carbonylation catalyst recycle system.

[0099] In some embodiments, the pressure in the carbonylation reactor is about 900 psig, and the temperature is about 70°C. In certain variations, the reactor is equipped with an external cooler (heat exchanger). In some variations, the carbonylation reaction achieves a selectivity of bPL above 99%.

[00100] With reference again to the exemplary system in FIG. **6**, a β-propiolactone product stream exits the outlet of the carbonylation reactor. The β-propiolactone product stream comprises bPL, solvent, unreacted EO and CO, carbonylation catalyst, and by-products, such as acetaldehyde by-product (ACH) and succinic anhydride (SAH). The β-propiolactone product stream may have any concentration of bPL, solvent, EO, CO carbonylation catalyst, ACH, and SAH described herein. For example, in some embodiments, the β-propiolactone product stream includes between about 2000 kg/hr bPL to about 40000 kg/hr bPL. In some

embodiments, the β-propiolactone product stream includes between about 30 kmol/hr bPL to about 550 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the β-propiolactone product stream can be about 0.1 to about 0.4. In some embodiments, the mole fraction of bPL in the β-propiolactone product stream can be about 0.1 to about 0.6. and more narrowly 0.1 to 0.4. The β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005 to 0.15, or at most about 0.1), unreacted carbon monoxide (in mass fraction of about 0.0005 to 0.04, or at most about 0.02), acetaldehyde (in mass fraction of about 0.0005 to 0.01, or at most about 0.02), succinic anhydride (in mass fraction of about 0.0005 to 0.005, or at most about 0.01), carbonylation catalyst (in about 40 to 640 kg/hr, or at most about 600 kg/hr; or a mass fraction of about 0.001 to 0.005, or at most about 0.004), and the remainder solvent. In some embodiments, the β-propiolactone product stream comprises carbonylation catalyst components (in about 40 to 640 kg/hr, or at most about 600 kg/hr; or a mass fraction of about 0.001 to 0.005, or at most about 0.004). In some embodiments, the β-propiolactone product stream from the β-propiolactone production system/production process can have a temperature of about 40°C or 50°C to about 100°C, and a pressure of about 1 bar to about 15 bar or more narrowly to 5 bar.

[00101] With reference again to the exemplary system in FIG. **6**, the β-propiolactone product stream is output from an outlet of the carbonylation reactor and enters an inlet of the ethylene oxide and carbon monoxide separator (labeled 'EO/CO' in FIG. **6**). In one embodiment, the ethylene oxide and carbon monoxide separator is a flash tank. The majority of the ethylene oxide and carbon monoxide is recovered from the carbonylation reaction stream and can be recycled back to the carbonylation reactor as a recycled ethylene oxide stream and a recycled carbon monoxide stream (labeled 'Recycle' in FIG. **6**), or sent for disposal (labeled 'Flare' in FIG. **6**). In some embodiments, at least 10% of the ethylene oxide and 80% of the carbon monoxide in the carbonylation reaction stream is recovered. The recycled carbon

monoxide stream can also include unreacted ethylene oxide (in about at most 250 kg/hr or a mass fraction of between about 0.05 to about 0.075), secondary reaction product acetaldehyde (in at most about 13 kg/hr or a mass fraction of about 0.001 to about 0.009), bPL (in at most about 0.19 kg/hr), and the remainder solvent (e.g., THF).

[00102] With reference again to the exemplary system in FIG. **6**, the β-propiolactone product stream is pumped into the carbonylation catalyst recycle system. In some variations, the ethylene oxide and carbon monoxide are disposed of using a method other than flare. For example, in one embodiment, the ethylene oxide and carbon monoxide recovered from the β-propiolactone product stream are disposed of using incineration.

[00103] With reference again to the exemplary system in FIG. **6**, the β-propiolactone product stream enters an inlet of the carbonylation catalyst recycling system. The carbonylation catalyst recycling system may be configured to isolate at least a portion of the carbonylation catalyst from the β-propiolactone product stream using any of the methods described herein, including, for example distillation, liquid-liquid extraction, ionic liquids, nanofiltration, ion exchange, or adsorption, or any combinations thereof. In some variations, the carbonylation catalyst recycling system includes a membrane separator. In certain variations, the membrane separator comprises a polymeric membrane, while in other variations the membrane separator comprises a ceramic membrane. In some variations, the membrane of the catalyst recycle system is configured to achieve between 90% and 100% rejection of the catalyst, and have permeability greater than 1. In some embodiments the membrane is achieves greater than 90%, 92%, 95%, 98%, or 99% rejection of the catalyst.

[00104] The carbonylation catalyst recycling system is configured to produce a recycled carbonylation catalyst stream (labeled 'Retentate' in FIG. **6**) comprising bPL, solvent, ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and carbonylation catalyst) and carbonylation catalyst, and a post-isolation β-propiolactone product stream (labeled 'Permeate'

in FIG. **6**) comprising bPL, solvent, ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and succinic anhydride) and trace amounts of carbonylation catalyst. In some embodiments, the post-isolation β-propiolactone product stream comprises trace amounts of carbonylation catalyst components. In some embodiments, trace amount is less than 1% by wt, less than 0.5% by wt, less than 0.01% by wt, less than 0.005% by wt, less than 0.001% by wt, or less than 0.0001% by wt. In certain embodiments, trace amount is below the detection threshold of the measurement method being used.

[00105] The recycled carbonylation catalyst stream may comprise any concentration of carbonylation catalyst, carbonylation catalyst components, and solvent disclosed herein. For example, in some embodiments, the mass fraction of carbonylation catalyst in the recycled carbonylation catalyst stream is about 0.005 to about 0.05. In some embodiments, the mass fraction of carbonylation catalyst components in the recycled carbonylation catalyst stream is about 0.0051 to about 0.05. In some embodiments, the mole fraction of carbonylation catalyst in the recycled carbonylation catalyst stream is about 0.0005 to about 0.05. In some embodiments, the mole fraction of carbonylation catalyst components in the recycled carbonylation catalyst stream is about 0.0005 to about 0.05. In some embodiments, the mass fraction of solvent in the recycled carbonylation catalyst stream is between 0.60 to about 0.99. In some embodiments, the mole fraction of solvent in the recycled carbonylation catalyst stream is between about 0.60 to about 0.99. In some embodiments, the recycled carbonylation catalyst stream can also include unreacted carbon monoxide (in at most about 15 kg/hr or a mass fraction of at most about 0.001), unreacted ethylene oxide (in at most about 330 kg/hr or a mass fraction of between 0.005 to 0.01), secondary reaction product acetaldehyde (in at most about 33 kg/hr or a mass fraction of at most about 0.001), secondary reaction product succinic anhydride (in at most about 30 kg/hr or a mass fraction of at most about 0.001), bPL (in at

most about 5450 kg/hr or a mass fraction of at most about 0.25). The recycled carbonylation catalyst stream is recycled back to the carbonylation reactor.

[00106] The post-isolation β-propiolactone product stream may have any concentration of bPL, solvent, ethylene oxide, carbon monoxide, by-products (such as acetaldehyde and succinic anhydride), carbonylation catalyst, or carbonylation catalyst components described herein. For example, in some embodiments, the post-isolation β-propiolactone product stream includes about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the post-isolation β-propiolactone product stream includes about 30 kmol/hr bPL to about 450 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1 to 0.4, or the mole fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1 to about 0.4. The post-isolation β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005 to 0.1), unreacted carbon monoxide (in mass fraction of about 0.0005 to 0.001, or at most about 0.002), acetaldehyde (in mass fraction of about 0.0005 to 0.001, or at most about 0.002), succinic anhydride (in mass fraction of about 0.0005 to 0.01, or at most about 0.02), carbonylation catalyst (in about 0 to 50 kg/hr, or at most about 20 kg/hr), carbonylation catalyst components (in about 0 to 50 kg/hr, or at most about 20 kg/hr) and the remainder solvent. In some embodiments, the post-isolation β-propiolactone product stream from the carbonylation catalyst recycling system can have a temperature of about 20°C to about 60°C. In some embodiments, the post-isolation β-propiolactone product stream can have a pressure of about 1 to about 5 bar.

[00107] With reference again to the exemplary system in FIG. **6**, the post-isolation β-propiolactone product stream may enter the inlet of the BPL purification system (labeled 'BPL Distillation' in FIG. **6**). In one variation, the BPL purification system comprises one or more distillation columns operating at or below atmospheric pressure configured to produce a

recovered solvent stream, and a production stream comprising purified bPL and trace amounts of carbonylation catalyst (labeled 'BPL/residual cat.' in FIG. **6**). The pressure is selected in such a way to achieve the temperature that reduces the decomposition of bPL. In some embodiments, the one or more distillation columns are operated at a pressure of about 0.15 bara and a temperature between about 80°C and about 120°C. In some embodiments, the distillation system is configured to produce a recycled solvent stream essentially free of ethylene oxide, carbon monoxide, acetaldehyde, and succinic anhydride.

[0100] With reference again to the exemplary system in FIG. **6**, the recovered solvent stream exits an outlet of the BPL purification system and may be fed back to the carbonylation reactor. In some variations, the concentration of H_2O and O_2 is reduced in the recycled solvent stream prior to being fed to the carbonylation reactor. The recovered solvent stream may have any concentration of H_2O and O_2 described herein when fed back to the carbonylation reactor. For example, in some embodiments, the concentration of H_2O and O_2 is less than about 500 ppm, less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, less than about 20 ppm, less than about 10 ppm, less than about 2 ppm, or less than about 1 ppm when fed back into the carbonylation reactor.

[0101] With reference again to the exemplary system in FIG. **6**, the production stream comprising purified bPL exits the outlet of the BPL purification system. The production stream may contain trace amounts of carbonylation catalyst, but is essentially free of solvent, ethylene oxide, carbon monoxide, acetaldehyde, and succinic anhydride. In some embodiments, the production stream contains a mass fraction of bPL of about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the production stream is about 0.90 to 1.0. In some embodiments, the remainder of the production stream includes secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or from 0 to 0.0015), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments,

the remainder of the production stream includes carbonylation catalyst components (in at most about 1000 ppm).

[0102] The production stream enters an inlet of the polypriolactone production system/production process. In the exemplary system depicted in FIG. **6**, the polypriolactone production system/production process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **6**). The polypriolactone production system/production process is configured to receive and output streams at any rate, concentration, temperature, or pressure described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or from 0 to about 0.015), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). The remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm).In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80°C to 120°C. In some embodiments, the production stream exiting the distillation process can be at a pressure of about 0.05 bar to about 0.15 bar. In some embodiments, the production stream entering the polymerization process can be at a pressure of at least about 0.05 bar, at least about 1 bar, or at least about 5 bar, or between about 0.05 bar and about 20 bar.

[0103] With reference again to the exemplary system in FIG. **6**, the polypropiolactone production system/production process is configured to operate in a continuous mode and achieves complete conversion of bPL in the production stream to PPL. A PPL product stream (labeled 'PPL/residual cat.' in FIG. **6**) exits an outlet of the polypropiolactone production system/production process, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises trace amount of carbonylation catalyst components.

[0104] In some embodiments, the polymerization process is configured to produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process is configured to produce about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0105] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or between 0 and 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or between 0 and 0.01) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the PPL product stream can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the PPL product stream can have a temperature between about 100°C to 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0106] With reference again to the exemplary system in FIG. **6**, the PPL product stream enters an inlet of the PPL purification system (labeled 'IER' in FIG. **6**). The PPL purification system can comprises and ion exchange resin (IER) configured to reduce the concentration of carbonylation catalyst in the PPL product stream. The cationic and anionic carbonylation catalyst species are recovered from the IER in the PPL purification system and can be

regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **6**). A post-purification PPL product stream exits an outlet of the PPL purification system and enters an inlet of the thermolysis reactor. The post-purification PPL product stream may have any concentration of compounds, temperature, or pressure described herein. For example, in some embodiments, the mass fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the post-purification PPL product stream can have a temperature between about 100°C to 140°C. In some embodiments, the post-purification PPL product stream can be at a pressure of at least about 0.001 bar.

[0107] With reference again to the exemplary system in FIG. **6**, a thermolysis reactor is configured to convert the post-purification PPL stream to a GAA product stream. In some embodiments, the temperature of the thermolysis reactor is between 140 °C or 160 °C and 300°C and the pressure is between 0.1 bara and 5 bara.

[0108] Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **6**) are separated from the GAA stream, exit an outlet of the thermolysis reactor, and sent to the incinerator for disposal (labeled 'Incinerator' in FIG. **6**).

[0109] A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 50°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 bar to about 1.5 bar.

[0110] The exemplary production system/production process depicted in FIG. **6** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA") to about 250 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0111] FIG. **7** provides an exemplary production system/production process where the PPL product stream and the GAA product stream are produced at the same location, at least a portion of the carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, and the conversion of bPL in the production stream to PPL in the polymerization reactor is incomplete, with recycling of bPL back to the polymerization reactor. The production system/production process shown in FIG. **7** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system as shown in FIG. **6**.

[0112] With reference again to the exemplary system in FIG. **7**, the production stream comprising purified bPL exits the outlet of the BPL purification system. The production stream may contain trace amounts of carbonylation catalyst, but is essentially free of solvent, ethylene oxide, carbon monoxide, acetaldehyde, and succinic anhydride. In some embodiments, the production stream contains a mass fraction of bPL of about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the production stream is about 0.90 to 1.0. In some embodiments, the remainder of the production stream includes secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the

remainder of the production stream includes carbonylation catalyst components (in at most about 1000 ppm).

[0113] With reference again to the exemplary system in FIG. **7**, the polypropiolactone production system/production process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **7**) and a BPL recycling system (labeled 'Distill/WFE' in FIG. **7**). The polypropiolactone production system/production process may be configured to receive and output streams at any rate, concentration, temperature, or pressure of production stream described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or 0 to 0.015) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80 to 120°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of about 0.05 bar to about 20 bar.

[0114] With reference again to the exemplary system in FIG. **7**, the PPL production system/production process is configured to operate in a continuous mode, achieving partial

conversion of bPL to PPL. The PPL production system/production process may be configured to achieve various levels of bPL conversion. For example, in some embodiments, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90% of the bPL in the production stream is converted to PPL. In some embodiments, about 50% to about 99% of the bPL in the production stream is converted to PPL. The partial polymerization stream exits the outlet of the polymerization reactor and enters the inlet of the BPL recycling system. The BPL recycling system is configured to separate unreacted bPL from the partial polymerization stream and recycle the bPL back into the polymerization reactor (labeled 'bPL' in FIG. **7**). In some embodiments, the BPL recycling system comprises one or more distillation columns, while in other embodiments the BPL recycling system comprises one or more wiped-film evaporators (WFE). A PPL product stream (labeled 'PPL/residual cat.' in FIG. **7**) exits the outlet of the BPL recycling system, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises PPL with trace amount of carbonylation catalyst components. In some embodiments, the polymerization process can produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process can produce about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0115] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or 0 to 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or from 0 to 0.01) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the PPL product stream can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the PPL product stream can

have a temperature between about 100 °C to 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0116] The PPL product stream enters the inlet of the PPL purification system (labeled 'IER' in FIG. **7**). In some variations, the PPL purification system may use an ion exchange resin (IER) to reduce the concentration of carbonylation catalyst in the PPL product stream. The cationic and anionic carbonylation catalyst species are recovered from the IER in the PPL purification system and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **7**). A post-purification PPL product stream exits an outlet of the PPL purification system and enters an inlet of the thermolysis reactor. The post-purification PPL product stream may have any concentration of compounds, temperature, or pressure described herein. For example, in some embodiments, the mass fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the post-purification PPL product stream can be about 0.90 to 1.0. In some embodiments, the post-purification PPL product stream can have a temperature between about 100°C to about 140°C. In some embodiments, the post-purification PPL product stream can be at a pressure of at least about 0.001 bar.

[0117] With reference again to the exemplary system in FIG. **7**, the glacial acrylic acid production system/production process is configured to convert the post-purification PPL stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **7**) are output via an outlet of the thermolysis reactor, and are sent to the incinerator for disposal (labeled 'Incinerator' in FIG. **7**). A GAA product stream exits an outlet of the thermolysis reactor, and may be condensed, further processed or stored. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary

reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 bar to about 1.5 bar.

[0118] The exemplary production system/production process depicted in FIG. **7** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA") to about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0119] FIG. **8** depicts an exemplary production system/production process where the PPL product stream and the GAA product stream are produced at the same location, carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor, the conversion of bPL to PPL in the polymerization process is complete with no recycling of bPL to the polymerization process, and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor. The production system/production process in FIG. **8** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system as shown in FIG. **6**.

[0120] With reference again to the exemplary system in FIG. **8**, the production stream exits the outlet of the BPL purification system and enters the inlet of the polymerization process. In the production system/production process depicted in FIG. **8**, the polymerization process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **8**). An inlet to the polymerization process may include any rate, concentration, temperature, or pressure of

production stream described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or 0 to 0.015), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm). In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80°C to about 120°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of about 0.05 bar to about 0.15 bar.

[0121] With reference again to the exemplary system in FIG. **8**, the polypropiolactone production system/production process is configured to operate in a continuous mode, achieving complete conversion of bPL in the production stream to PPL. A PPL product stream (labeled 'PPL/residual cat.' in FIG. **8**) exits the polymerization process outlet, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises PPL with trace amount of carbonylation catalyst components.

[0122] In some embodiments, the polymerization process can produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process can produce about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0123] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or from 0 to 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or from 0 to 0.01), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the PPL product stream can have a temperature between about 100°C to about 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0124] With reference again to the exemplary system in FIG. **8**, the PPL product stream enters the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **8**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **8**) comprising ion exchange resin (IER) which may be used in some embodiments may be useful. The IER is configured to reduce the concentration of carbonylation catalyst in the stream of high boiling organic impurities. In some embodiments, the concentration of carbonylation catalyst in the stream of high boiling organic impurities is between 100 ppm to 1000 ppm before entering the purification system, and is less than 50 ppm, less than 20 ppm, or less than 5 ppm after exiting the purification system.

[0125] The cationic and anionic carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **8**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. A GAA product stream exits an outlet of the thermolysis

reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0126] The exemplary production system/production process depicted in FIG. **8** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA to about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0127] FIG. **9** depicts an exemplary production system/production process where the PPL product stream and the GAA product stream are produced at the same location, carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor, the conversion of bPL to PPL in the polymerization process is in complete and bPL is recycled back to the polymerization process, and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor. The production system/production process in FIG. **9** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system as shown in FIG. **6**.

[0128] With reference again to the exemplary system in FIG. **9**, the production stream comprising purified bPL exits the outlet of the BPL purification system. The production stream

contains trace amounts of carbonylation catalyst, but is essentially free of THF, EO, CO, ACH, and SAH. The production stream is fed forward and enters an inlet of the polymerization process. The polymerization process comprises a polymerization reactor (labeled 'Polymerization' in FIG. **9**) and a BPL recycling system (labeled 'Distill/WFE' in FIG. **9**). An inlet to the polymerization process may include any rate, concentration, temperature, or pressure of production stream described herein. For example, in one embodiment, the inlet to the polymerization process can include about 2000 kg/hr bPL to about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 25 kmol/hr bPL to about 500 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be about 0.90 to 1.0. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be from about 0.90 to 1.0. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, or from 0 to 0.015) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. In some embodiments, the production stream entering the polymerization process can have a temperature between about 80°C to 120°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of about 0.05 bar to about 20 bar.

[0129] With reference again to the exemplary system in FIG. **9**, the polypropiolactone production system/production process is configured to operate in a continuous mode, achieving partial conversion of bPL in the production stream to PPL. The polypropiolactone production system/production process may be configured to achieve various levels of bPL conversion. For example, in some embodiments, at least 40%, at least 50%, at least 60%, at least 70%, at least

80%, or at least 90% of the bPL in the production stream is converted to PPL. In some embodiments, about 50% to about 95% of the bPL in the production stream is converted to PPL. In some embodiments, about 50% to about 99% of the bPL in the production stream is converted to PPL. The partial polymerization stream exits the outlet of the polymerization reactor and enters the inlet of the BPL recycling system. The BPL recycling system is configured to separate unreacted bPL from the partial polymerization stream and recycle the bPL back into the polymerization reactor (labeled 'bPL' in FIG. **9**). In some embodiments, the BPL recycling system comprises one or more distillation columns, while in other embodiments the BPL recycling system comprises one or more wiped-film evaporators (WFE). A PPL product stream (labeled 'PPL/residual cat.' in FIG. **9**) exits the outlet of the BPL recycling system, and comprises PPL with trace amount of carbonylation catalyst. In some embodiments, the PPL product stream comprises PPL with trace amount of carbonylation catalyst components. In some embodiments, the polymerization process is configured to produce about 2000 kg/hr PPL to about 35000 kg/hr PPL. In some embodiments, the polymerization process is configured to produce from about 25 kmol/hr PPL to about 500 kmol/hr PPL.

[0130] In some embodiments, the mass fraction of PPL in the PPL product stream can be about 0.90 to 1.0. In some embodiments, the mole fraction of PPL in the PPL product stream can be about 0.90 to 1.0. The remainder of the PPL product stream can include unreacted bPL (in mole fraction of at most about 0.02, or from 0 to 0.02), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, or from 0 to 0.01), leftover solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some embodiments, the PPL product stream can have a temperature between about 100°C to 140°C. In some embodiments, the PPL product stream can be at a pressure of at least about 0.001 bar.

[0131] With reference again to the exemplary system in FIG. **9**, the PPL product stream enters the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **9**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **9**) comprising ion exchange resin (IER). The IER is configured to reduce the concentration of carbonylation catalyst (or components thereof) in the stream of high boiling organic impurities. The cationic and anionic carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **9**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and leftover solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0132] The exemplary production system/production process depicted in FIG. 9 may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA and about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0133] FIG. **10** depicts another exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, the polymerization reactor achieves complete conversion of bPL in the production stream to PPL and bPL is not recycled back to the polymerization reactor. The production system/production process in FIG. **10** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, polymerization process, PPL purification system, and regeneration or disposal of carbonylation catalyst components as shown in FIG. **6**.

[0134] With reference again to the exemplary system in FIG. **10**, the post-purification PPL product stream exits an outlet of the PPL purification system and is pelletized, extruded, flaked, powdered, or granulated by any means known in the art in essentially dry atmosphere. The solid post-purification PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid post-purification PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid post-purification PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the post-isolation PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **10**) are output via an outlet of the thermolysis reactor and sent to an incinerator for disposal (labeled 'Incinerator' in FIG. **10**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product

stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0135] The exemplary production system/production process depicted in FIG. **10** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA and about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0136] FIG. **11** depicts an exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are removed from the PPL product stream prior to entering the thermolysis reactor, the polymerization reactor achieves incomplete conversion of bPL in the production stream to PPL and bPL is recycled back to the polymerization reactor. The production system/production process in FIG. **11** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, polymerization process, PPL purification system, and regeneration or disposal of carbonylation catalyst components as shown in FIG. **7**.

[0137] With reference again to the exemplary system in FIG. **11**, the post-purification PPL product stream exits an outlet of the PPL purification system and is pelletized, extruded, flaked, powdered, or granulated by means known in the art in essentially dry atmosphere. The solid

post-purification PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid post-purification PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid post-purification PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the post-isolation PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **11**) are output via an outlet of the thermolysis reactor and sent to an incinerator for disposal (labeled 'Incinerator' in FIG. **11**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0138] The exemplary production system/production process depicted in FIG. **11** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA to about 250 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0139] FIG. **12** depicts another exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor; the polymerization reactor achieves complete conversion of bPL in the production stream to PPL and bPL is not recycled back to the polymerization reactor; and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor. The production system/production process in FIG. **12** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, and polymerization process as shown in FIG. **8**.

[0140] With reference again to the exemplary system in FIG. **12**, the PPL product stream exits an outlet of the polymerization process and is pelletized, extruded, flaked, powdered, or granulated by means known in the art in essentially dry atmosphere. The solid PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **12**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **12**) comprising ion exchange and which is an example of one separation the may be employed. The IER is configured to reduce the concentration of carbonylation catalyst (or components thereof) in the stream of high boiling organic impurities. The cationic and anionic

carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **12**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. In preferred embodiment the temperature is controlled to limit the risk of autopolymerization of acrylic acid. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0141] The exemplary production system/production process depicted in FIG. **12** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), or between about 25 KTA and about 400 KTA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA to about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0142] FIG. **13** depicts an exemplary production system/production process where the PPL product stream is produced at a first location, then isolated, packaged, and shipped to a second location where the GAA product stream is produced; carbonylation catalyst or components thereof are not removed from the PPL product stream prior to entering the thermolysis reactor; the polymerization reactor achieves incomplete conversion of bPL in the production stream to PPL and bPL is recycled back to the polymerization reactor; and carbonylation catalyst or components thereof are removed from the organic heavies produced by the thermolysis reactor.

The production system/production process in FIG. **13** has the same configuration of carbonylation reactor, CO catalyst recycling, EO/CO recycling and BPL purification system, and polymerization process as shown in FIG. **9**.

[0143] With reference again to the exemplary system in FIG. **13**, the PPL product stream exits an outlet of the polymerization process and is pelletized, extruded, flaked, powdered, or granulated by means known in the art in essentially dry atmosphere. The solid PPL product stream is then fed forward to packaging, and becomes ready to be shipped to the location of the GAA production system/production process. The packaging used to ship the solid PPL product stream is selected to minimize the moisture absorption by solid PPL. At the location of the GAA production system/production process, the essentially pure, essentially dry solid PPL product stream is unpackaged in a way to minimize introduction of moisture, and then fed in a solid or molten form to the inlet of the thermolysis reactor. The thermolysis reactor is configured to convert the PPL product stream to a GAA stream. Traces of high boiling organic impurities (labeled 'Organic Heavies' in FIG. **13**) are output via an outlet of the thermolysis reactor. The stream of high boiling organic impurities enters a purification system (labeled 'IER' in FIG. **13**) comprising ion exchange resin (IER). The IER is configured to reduce the concentration of carbonylation catalyst (or components thereof) in the stream of high boiling organic impurities. The cationic and anionic carbonylation catalyst species are recovered from the IER and can be regenerated to obtain catalyst available for recycle to the carbonylation reactor or be disposed of (labeled 'Regenerate/Dispose' in FIG. **13**). A GAA product stream exits an outlet of the thermolysis reactor for storage or further processing. The GAA product stream comprises essentially pure GAA. The GAA product stream may exit an outlet of the thermolysis reactor at any rate, concentration, temperature, or pressure described herein. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product stream

can have a temperature between about 15°C to about 60°C. In some embodiments, the GAA product stream can be at a pressure of about 0.5 to about 1.5 bar.

[0144] The exemplary production system/production process depicted in FIG. **13** may produce GAA at any rate described herein. For example, in some embodiments, the system produces at least about 25 kilo tons per annum ("KTA"), at least about 100 KTA, at least about 110 KTA, at least about 120 KTA, at least about 130 KTA, at least about 140 KTA, at least about 150 KTA, at least about 160 KTA, at least about 170 KTA, at least about 180 KTA, at least about 190 KTA, at least about 200 KTA, at least about 250 KTA, at least about 300 KTA, at least about 350 KTA, at least about 400 KTA, and in some variations that may be combined with any of the preceding variations, up to about 400 KTA, for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, or between about 2000 kg/hr GAA and about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 25 kmol/hr GAA to about 500 kmol/hr GAA.

[0145] It should be understood that while FIGS. **6-13** depict process configurations comprising certain steps and unit operations, in other embodiments of the methods described herein the process configuration contains fewer steps, more steps, fewer unit operations, or more unit operations. For example, in some variations, the permeate stream is treated to remove at least a portion of the trace carbonylation catalyst prior to the BPL purification train. In certain variations, it may be possible toremove of at least a portion of the trace carbonylation catalyst from the permeate with an ion exchange resin. Thus, in certain embodiments, the process configurations in FIGS. **6-13** includes the additional step of removing at least a portion of the trace carbonylation catalyst from the permeate using IER, before the permeate enters the BPL purification train. In some embodiments, the systems depicted in FIGS. **6-13** and described herein include a purification system with IER before prior to the BPL purification

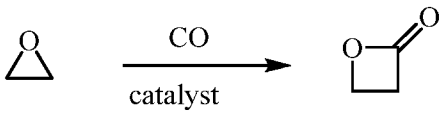
train. In other embodiments, the systems include a purification system with IER prior to the BPL purification train and use a heterogeneous polymerization catalyst in the polymerization process. In some embodiments, the systems do not have a purification system after the polymerization process.

[0146] Each of the unit operations in the production system/production processs for acrylic acid and precursors thereof are described in further detail below.

β-Propiolactone Production system/production process (i.e., carbonylation reaction system)

[0147] FIG. **14** illustrates an exemplary embodiment of the production system/production process disclosed herein. FIG. **14** contains carbonylation reaction system 1413 (i.e., β-propiolactone production system/production process), catalyst isolation system 1415, BPL purification system 1417, polymerization reaction system 1419, and thermolysis system 1421.

[0148] In the carbonylation reaction system, Ethylene oxide can be converted to β-propiolactone by a carbonylation reaction, as depicted in the reaction scheme below.



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[0149] Water and oxygen can damage the carbonylation catalyst. The feed streams (i.e., EO, CO, solvent, carbonylation catalyst) to the carbonylation reaction system should be substantially dry (i.e., have a water content below 5 ppm) and be oxygen free (i.e., have an oxygen content below 5 ppm). As such, the feed streams and/or storage tanks and/or feed tank can have sensors on them in order to determine the composition of the stream/tank to make sure that they have a low enough oxygen and water content. In some embodiments, the feed streams can be purified such as by adsorption to reduce the water and oxygen content in the streams fed to the carbonylation reaction system. In some embodiments, prior to running the production system/production process, the tubes, apparatuses, and other flow paths can be

purged with an inert gas or carbon monoxide to minimize exposure to oxygen or water in the production system/production process.

Ethylene Oxide Source

[0150] FIG. **14** includes ethylene oxide source 1402 that can feed fresh ethylene oxide in ethylene oxide stream 1406 to carbonylation reaction system inlet 1409. Inlet 1409 can be one inlet to the carbonylation reaction system or multiple inlets. Ethylene oxide can be fed as a liquid using a pump or any other means known to those of ordinary skill in the art. In addition, the ethylene oxide source can be maintained under an inert atmosphere. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at least about 1000 kg/hr, at least about 1500 kg/hr, at least about 2000 kg/hr, at least about 2070 kg/hr, or at least about 2500 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 1000 kg/hr to about 2500 kg/hr, at least about 1500 kg/hr to about 2500 kg/hr, at least about 2000 kg/hr to about 2500 kg/hr, or at least about 2070 kg/hr to about 2500 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source from about 1000 kg/hr to about 25000 kg/hr, about 1500 kg/hr to about 25000 kg/hr, about 2000 kg/hr to about 25000 kg/hr, about 2500 kg/hr to about 25000 kg/hr, about 5000 kg/hr to about 25000 kg/hr, about 7500 kg/hr to about 25000 kg/hr, about 10000 kg/hr to about 25000 kg/hr, about 12500 kg/hr to about 25000 kg/hr, about 15000 kg/hr to about 25000 kg/hr, about 17500 kg/hr to about 25000 kg/hr, about 20000 kg/hr to about 25000 kg/hr, or about 22500 kg/hr to about 25000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 1000 kg/hr, about 1500 kg/hr, about 2000 kg/hr, about 2070 kg/hr, about 2500 kg/hr, about 3000 kg/hr, about 3500 kg/hr, about 4000 kg/hr, about 4500 kg/hr, about 5000 kg/hr, 7500 kg/hr, about 10000 kg/hr, about 12500 kg/hr, about 15000 kg/hr, about 17500 kg/hr, about

20000 kg/hr, about 22500 kg/hr, or about 25000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at least about 30 kmol/hr, at least about 35 kmol/hr, at least about 40 kmol/hr, at least about 47 kmol/hr, at least about 50 kmol/hr, at least about 100 kmol/hr, at least about 200 kmol/hr, at least about 300 kmol/hr, at least about 400 kmol/hr, or at least about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 30 kmol/hr to about 500 kmol/hr, about 35 kmol/hr to about 500 kmol/hr, about 40 kmol/hr to about 500 kmol/hr, about 47 kmol/hr to about 500 kmol/hr, about 50 kmol/hr to about 500 kmol/hr, about 100 kmol/hr to about 500 kmol/hr, about 200 kmol/hr to about 500 kmol/hr, about 300 kmol/hr to about 500 kmol/hr, or about 400 kmol/hr to about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at about 30 kmol/hr, about 35 kmol/hr, about 40 kmol/hr, about 47 kmol/hr, about 50 kmol/hr, about 70 kmol/hr, about 80 kmol/hr about 90 kmol/hr, about 100 kmol/hr, about 150 kmol/hr, about 200 kmol/hr, about 250 kmol/hr, about 300 kmol/hr, about 350 kmol/hr, about 400 kmol/hr, about 450 kmol/hr, or about 500 kmol/hr. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at a temperature between about 10-30°C, between about 15-25°C, or about 20°C. In some embodiments, the inlet to the carbonylation reaction system can receive ethylene oxide from an ethylene oxide source at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Carbonylation Catalyst Source

[0151] Numerous carbonylation catalysts known in the art are suitable for (or can be adapted to) methods of the present invention. For example, in some embodiments, the carbonylation methods utilize a metal carbonyl-Lewis acid catalyst such as those described in U.S. Patent No. 6,852,865. In other embodiments, the carbonylation step is performed with

one or more of the carbonylation catalysts disclosed in U.S. Patent Application Serial Nos. 10/820,958; and 10/586,826. In other embodiments, the carbonylation step is performed with one or more of the catalysts disclosed in U.S. Patent Nos. 5,310,948; 7,420,064; and 5,359,081. Additional catalysts for the carbonylation of epoxides are discussed in a review in Chem. Commun., 2007, 657–674. The entirety of each of the preceding references is incorporated herein by reference.

[0152] In some embodiments, the carbonylation catalyst includes a metal carbonyl compound. Typically, a single metal carbonyl compound is provided, but in some embodiments, mixtures of two or more metal carbonyl compounds are provided. Thus, when a provided metal carbonyl compound "comprises", e.g., a neutral metal carbonyl compound, it is understood that the provided metal carbonyl compound can be a single neutral metal carbonyl compound, or a neutral metal carbonyl compound in combination with one or more metal carbonyl compounds. Preferably, the provided metal carbonyl compound is capable of ring-opening an epoxide and facilitating the insertion of CO into the resulting metal carbon bond. Metal carbonyl compounds with this reactivity are well known in the art and are used for laboratory experimentation as well as in industrial processes such as hydroformylation.

[0153] In some embodiments, a provided metal carbonyl compound comprises an anionic metal carbonyl moiety. In other embodiments, a provided metal carbonyl compound comprises a neutral metal carbonyl compound. In some embodiments, a provided metal carbonyl compound comprises a metal carbonyl hydride or a hydrido metal carbonyl compound. In some embodiments, a provided metal carbonyl compound acts as a pre-catalyst which reacts *in situ* with one or more reaction components to provide an active species different from the compound initially provided. Such pre-catalysts are specifically encompassed as it is recognized that the active species in a given reaction may not be known with certainty; thus

the identification of such a reactive species *in situ* does not itself depart from the spirit or teachings of the present disclosure.

[0154] In some embodiments, the metal carbonyl compound comprises an anionic metal carbonyl species. In some embodiments, such anionic metal carbonyl species have the general formula $[Q_dM'_e(CO)_w]^{y-}$, where Q is any ligand and need not be present, M' is a metal atom, *d* is an integer between 0 and 8 inclusive, *e* is an integer between 1 and 6 inclusive, *w* is a number such as to provide the stable anionic metal carbonyl complex, and *y* is the charge of the anionic metal carbonyl species. In some embodiments, the anionic metal carbonyl has the general formula $[QM'(CO)_w]^{y-}$, where Q is any ligand and need not be present, M' is a metal atom, *w* is a number such as to provide the stable anionic metal carbonyl, and *y* is the charge of the anionic metal carbonyl.

[0155] In some embodiments, the anionic metal carbonyl species include monoanionic carbonyl complexes of metals from groups 5, 7 or 9 of the periodic table or dianionic carbonyl complexes of metals from groups 4 or 8 of the periodic table. In some embodiments, the anionic metal carbonyl compound contains cobalt or manganese. In some embodiments, the anionic metal carbonyl compound contains rhodium. Suitable anionic metal carbonyl compounds include, but are not limited to: $[Co(CO)_4]^-$, $[Ti(CO)_6]^{2-}$ $[V(CO)_6]^-$ $[Rh(CO)_4]^-$, $[Fe(CO)_4]^{2-}$ $[Ru(CO)_4]^{2-}$, $[Os(CO)_4]^{2-}$ $[Cr_2(CO)_{10}]^{2-}$ $[Fe_2(CO)_8]^{2-}$ $[Tc(CO)_5]^-$ $[Re(CO)_5]^-$and $[Mn(CO)_5]^-$. In some embodiments, the anionic metal carbonyl comprises $[Co(CO)_4]^-$. In some embodiments, a mixture of two or more anionic metal carbonyl complexes may be present in the carbonylation catalysts used in the methods.

[0156] The term "such as to provide a stable anionic metal carbonyl" for $[Q_dM'_e(CO)_w]^{y-}$ is used herein to mean that $[Q_dM'_e(CO)_w]^{y-}$ is a species characterizable by analytical means, e.g., NMR, IR, X-ray crystallography, Raman spectroscopy and/or electron spin resonance (EPR) and isolable in catalyst form in the presence of a suitable cation or a species formed *in*

situ. It is to be understood that metals which can form stable metal carbonyl complexes have known coordinative capacities and propensities to form polynuclear complexes which, together with the number and character of optional ligands Q that may be present and the charge on the complex will determine the number of sites available for CO to coordinate and therefore the value of *w*. Typically, such compounds conform to the "18-electron rule". Such knowledge is within the grasp of one having ordinary skill in the arts pertaining to the synthesis and characterization of metal carbonyl compounds.

[0157] In embodiments where the provided metal carbonyl compound is an anionic species, one or more cations must also necessarily be present. In some variations, no particular constraints on the identity of such cations. In some embodiments, the cation associated with an anionic metal carbonyl compound comprises a reaction component of another category described herein. For example, in some embodiments, the metal carbonyl anion is associated with a cationic Lewis acid. In other embodiments a cation associated with a provided anionic metal carbonyl compound is a simple metal cation such as those from Groups 1 or 2 of the periodic table (e.g., Na^+, Li^+, K^+, Mg^{2+} and the like). In other embodiments a cation associated with a provided anionic metal carbonyl compound is a bulky non electrophilic cation such as an 'onium salt' (e.g., Bu_4N^+, PPN^+, Ph_4P^+ Ph_4As^+, and the like). In other embodiments, a metal carbonyl anion is associated with a protonated nitrogen compound (e.g., a cation may comprise a compound such as MeTBD-H^+, DMAP-H^+, DABCO-H^+, DBU-H^+ and the like). In some embodiments, compounds comprising such protonated nitrogen compounds are provided as the reaction product between an acidic hydrido metal carbonyl compound and a basic nitrogen-containing compound (e.g., a mixture of DBU and $HCo(CO)_4$).

[0158] In some embodiments, a catalyst utilized in the methods described herein comprises a neutral metal carbonyl compound. In some embodiments, such neutral metal carbonyl compounds have the general formula $Q_dM'_e(CO)_{w'}$, where Q is any ligand and need not be

present, M' is a metal atom, *d* is an integer between 0 and 8 inclusive, e is an integer between 1 and 6 inclusive, and *w'* is a number such as to provide the stable neutral metal carbonyl complex. In some embodiments, the neutral metal carbonyl has the general formula $QM'(CO)_{w'}$. In some embodiments, the neutral metal carbonyl has the general formula $M'(CO)_{w'}$. In some embodiments, the neutral metal carbonyl has the general formula $QM'_2(CO)_{w'}$. In some embodiments, the neutral metal carbonyl has the general formula $M'_2(CO)_{w'}$. Suitable neutral metal carbonyl compounds include, but are not limited to: $Ti(CO)_7$; $V_2(CO)_{12}$; $Cr(CO)_6$; $Mo(CO)_6$; $W(CO)_6$ $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ $Fe(CO)_5$, $Ru(CO)_5$ and $Os(CO)_5$ $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Ir_4(CO)_{12}$ $Co_2(CO)_8$ $Ni(CO)_4$.

[0159] The term "such as to provide a stable neutral metal carbonyl" for $Q_dM'_e(CO)_{w'}$ is used herein to mean that $Q_dM'_e(CO)_{w'}$ is a species characterizable by analytical means, e.g., NMR, IR, X-ray crystallography, Raman spectroscopy and/or electron spin resonance (EPR) and isolable in pure form or a species formed *in situ*. It is to be understood that metals which can form stable metal carbonyl complexes have known coordinative capacities and propensities to form polynuclear complexes which, together with the number and character of optional ligands Q that may be present will determine the number of sites available for CO to coordinate and therefore the value of *w'*. Typically, such compounds conform to stoichiometries conforming to the "18-electron rule". Such knowledge is within the grasp of one having ordinary skill in the arts pertaining to the synthesis and characterization of metal carbonyl compounds.

[0160] In some embodiments, no ligands Q are present on the metal carbonyl compound. In other embodiments, one or more ligands Q are present on the metal carbonyl compound. In some embodiments, where Q is present, each occurrence of Q is selected from the group consisting of phosphine ligands, amine ligands, cyclopentadienyl ligands, heterocyclic ligands,

nitriles, phenols, and combinations of two or more of these. In some embodiments, one or more of the CO ligands of any of the metal carbonyl compounds described above is replaced with a ligand Q. In some embodiments, Q is a phosphine ligand. In some embodiments, Q is a triaryl phosphine. In some embodiments, Q is trialkyl phosphine. In some embodiments, Q is a phosphite ligand. In some embodiments, Q is an optionally substituted cyclopentadienyl ligand. In some embodiments, Q is cp. In some embodiments, Q is cp*. In some embodiments, Q is an amine or a heterocycle.

[0161] In some embodiments, the carbonylation catalyst utilized in the methods described above further includes a Lewis acidic component. In some embodiments, the carbonylation catalyst includes an anionic metal carbonyl complex and a cationic Lewis acidic component. In some embodiments, the metal carbonyl complex includes a carbonyl cobaltate and the Lewis acidic co-catalyst includes a metal-centered cationic Lewis acid. In some embodiments, an included Lewis acid comprises a boron compound.

[0162] In some embodiments, where an included Lewis acid comprises a boron compound, the boron compound comprises a trialkyl boron compound or a triaryl boron compound. In some embodiments, an included boron compound comprises one or more boron-halogen bonds. In some embodiments, where an included boron compound comprises one or more boron-halogen bonds, the compound is a dialkyl halo boron compound (e.g., R_2BX), a dihalo monoalkyl compound (e.g., RBX_2), an aryl halo boron compound (e.g., Ar_2BX or $ArBX_2$), or a trihalo boron compound (e.g., BCl_3 or BBr_3), wherein each R is an alkyl group; each X is a halogen; and each Ar is an aromatic group.

[0163] In some embodiments, where the included Lewis acid comprises a metal-centered cationic Lewis acid, the Lewis acid is a cationic metal complex. In some embodiments, the cationic metal complex has its charge balanced either in part, or wholly by one or more anionic metal carbonyl moieties. Suitable anionic metal carbonyl compounds include those described

above. In some embodiments, there are 1 to 17 such anionic metal carbonyls balancing the charge of the metal complex. In some embodiments, there are 1 to 9 such anionic metal carbonyls balancing the charge of the metal complex. In some embodiments, there are 1 to 5 such anionic metal carbonyls balancing the charge of the metal complex. In some embodiments, there are 1 to 3 such anionic metal carbonyls balancing the charge of the metal complex.

[0164] In some embodiments, where carbonylation catalysts used in systems and methods described herein include a cationic metal complex, the metal complex has the formula $[(L^c)_vM_b]^{z+}$, where:

L^c is a ligand where, when two or more L^c are present, each may be the same or different;

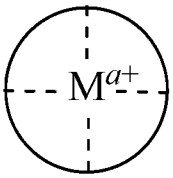
M is a metal atom where, when two M are present, each may be the same or different;

v is an integer from 1 to 4 inclusive;

b is an integer from 1 to 2 inclusive; and

z is an integer greater than 0 that represents the cationic charge on the metal complex.

[0165] In some embodiments, provided Lewis acids conform to structure **I**:



I

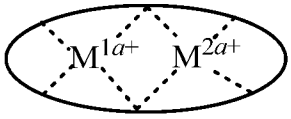
wherein:

 is a multidentate ligand;

M is a metal atom coordinated to the multidentate ligand;

a is the charge of the metal atom and ranges from 0 to 2; and

In some embodiments, provided metal complexes conform to structure **II**:



II

Where a is as defined above (each a may be the same or different), and

M^1 is a first metal atom;

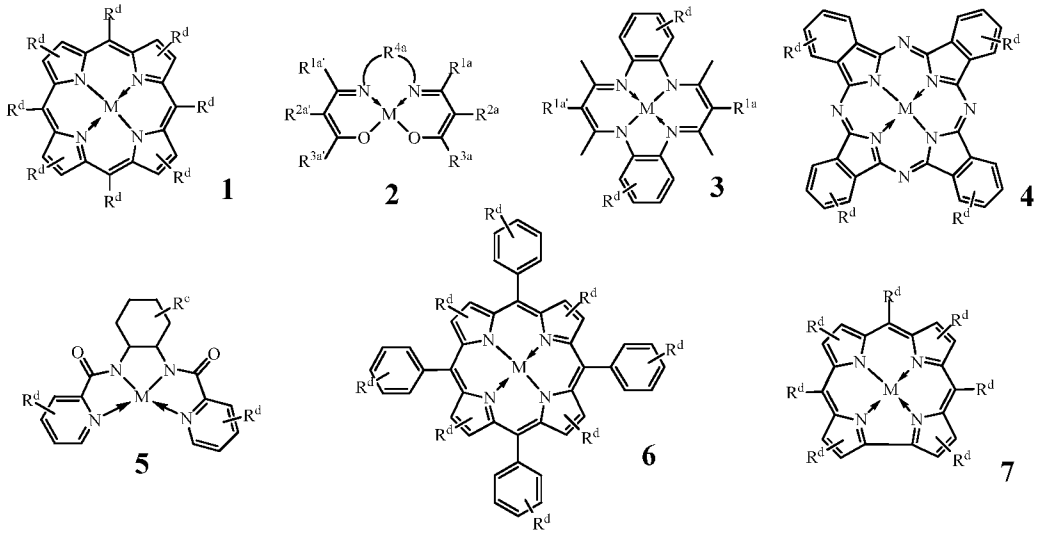
M^2 is a second metal atom;

 comprises a multidentate ligand system capable of coordinating both metal atoms.

[0166] For sake of clarity, and to avoid confusion between the net and total charge of the metal atoms in complexes **I** and **II** and other structures herein, the charge (a^+) shown on the metal atom in complexes **I** and **II** above represents the *net* charge on the metal atom after it has satisfied any anionic sites of the multidentate ligand. For example, if a metal atom in a complex of formula **I** were Cr(III), and the ligand were porphyrin (a tetradentate ligand with a charge of -2), then the chromium atom would have a net charge of +1, and a would be 1.

[0167] Suitable multidentate ligands include, but are not limited to: porphyrin derivatives **1**, salen derivatives **2**, dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives **3**, phthalocyaninate derivatives **4**, derivatives of the Trost ligand **5**, tetraphenylporphyrin derivatives **6**, and corrole derivatives **7**. In some embodiments, the multidentate ligand is a salen derivative. In other embodiments, the multidentate ligand is a porphyrin derivative. In other embodiments, the multidentate ligand is a tetraphenylporphyrin derivative. In other

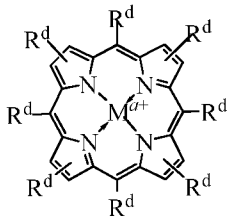
embodiments, the multidentate ligand is a corrole derivative.



,

where each of R^c, R^d, R^{1a}, R^{2a}, R^{3a}, R^{4a}, $R^{1a'}$, $R^{2a'}$, $R^{3a'}$, and M, is as defined and described in the classes and subclasses herein.

[0168] In some embodiments, Lewis acids provided carbonylation catalysts used in systems and methods described herein comprise metal-porphinato complexes. In some embodiments, the moiety  has the structure:



where each of M and *a* is as defined above and described in the classes and subclasses herein, and

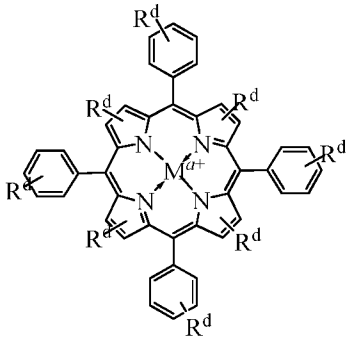
R^d at each occurrence is independently hydrogen, halogen, $-OR^4$, $-NR^y_2$, $-SR^y$, -CN, $-NO_2$, $-SO_2R^y$, $-SOR^y$, $-SO_2NR^y_2$; -CNO, $-NR^ySO_2R^y$, -NCO, $-N_3$, $-SiR^y_3$; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group

consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur, where two or more R^d groups may be taken together to form one or more optionally substituted rings,

each R^y is independently hydrogen, an optionally substituted group selected the group consisting of acyl; carbamoyl, arylalkyl; 6- to 10-membered aryl; C_{1-12} aliphatic; C_{1-12} heteroaliphatic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; an oxygen protecting group; and a nitrogen protecting group; two R^y on the same nitrogen atom are taken with the nitrogen atom to form an optionally substituted 4- to 7-membered heterocyclic ring having 0-2 additional heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; and

each R^4 is independently is a hydroxyl protecting group or R^y.

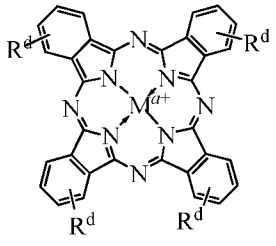
[0169] In some embodiments, the moiety  has the structure:



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where M, *a* and R^d are as defined above and in the classes and subclasses herein.

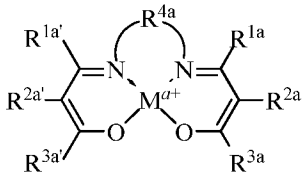
In some embodiments, the moiety  has the structure:



,

where M, *a* and R^d are as defined above and in the classes and subclasses herein.

[0170] In some embodiments, Lewis acids included in carbonylation catalysts used in systems and methods described herein comprise metallo salenate complexes. In some embodiments, the moiety  has the structure:



,

wherein:

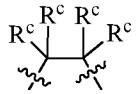
M, and *a* are as defined above and in the classes and subclasses herein.

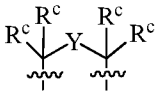
R^{1a}, $R^{1a'}$, R^{2a}, $R^{2a'}$, R^{3a}, and $R^{3a'}$ are independently hydrogen, halogen, $-OR^4$, $-NR^y_2$, $-SR^y$, -CN, $-NO_2$, $-SO_2R^y$, $-SOR^y$, $-SO_2NR^y_2$; -CNO, $-NR^ySO_2R^y$, -NCO, $-N_3$, $-SiR^y_3$; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; wherein each R^4,

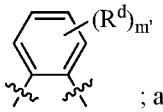
and R^y is independently as defined above and described in classes and subclasses herein,

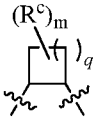
wherein any of ($R^{2a'}$ and $R^{3a'}$), (R^{2a} and R^{3a}), (R^{1a} and R^{2a}), and ($R^{1a'}$ and $R^{2a'}$) may optionally be taken together with the carbon atoms to which they are attached to form one or more rings which may in turn be substituted with one or more R^y groups; and

R^{4a} is selected from the group consisting of:

e) 

f) 

g)  ; and

h)  , where

R^c at each occurrence is independently hydrogen, halogen, $-OR^4$, $-NR^y_2$, $-SR^y$, -CN, $-NO_2$, $-SO_2R^y$, $-SOR^y$, $-SO_2NR^y_2$; -CNO, $-NR^ySO_2R^y$, -NCO, $-N_3$, $-SiR^y_3$; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur;

where:

two or more R^c groups may be taken together with the carbon atoms to which they are attached and any intervening atoms to form one or more rings;

when two R^c groups are attached to the same carbon atom, they may be taken together along with the carbon atom to which they are attached to form a moiety selected from the group consisting of: a 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, an imine; and an optionally substituted alkene;

where R^4 and R^y are as defined above and in classes and subclasses herein;

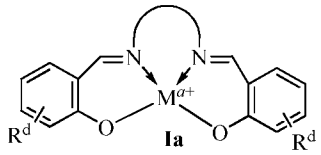
Y is a divalent linker selected from the group consisting of: $–NR^y$-, -$N(R^y)C(O)$-, -$C(O)NR^y$-, –O-, –C(O)-, –OC(O)-, -C(O)O-, -S-, -SO-, -SO_2-, -C(=S) -, -$C(=NR^y)$-, -N=N-; a polyether; a C_3 to C_8 substituted or unsubstituted carbocycle; and a C_1 to C_8 substituted or unsubstituted heterocycle;

m' is 0 or an integer from 1 to 4, inclusive;

q is 0 or an integer from 1 to 4, inclusive; and

x is 0, 1, or 2.

[0171] In some embodiments, a provided Lewis acid comprises a metallo salen compound, as shown in formula **Ia**:



Ia

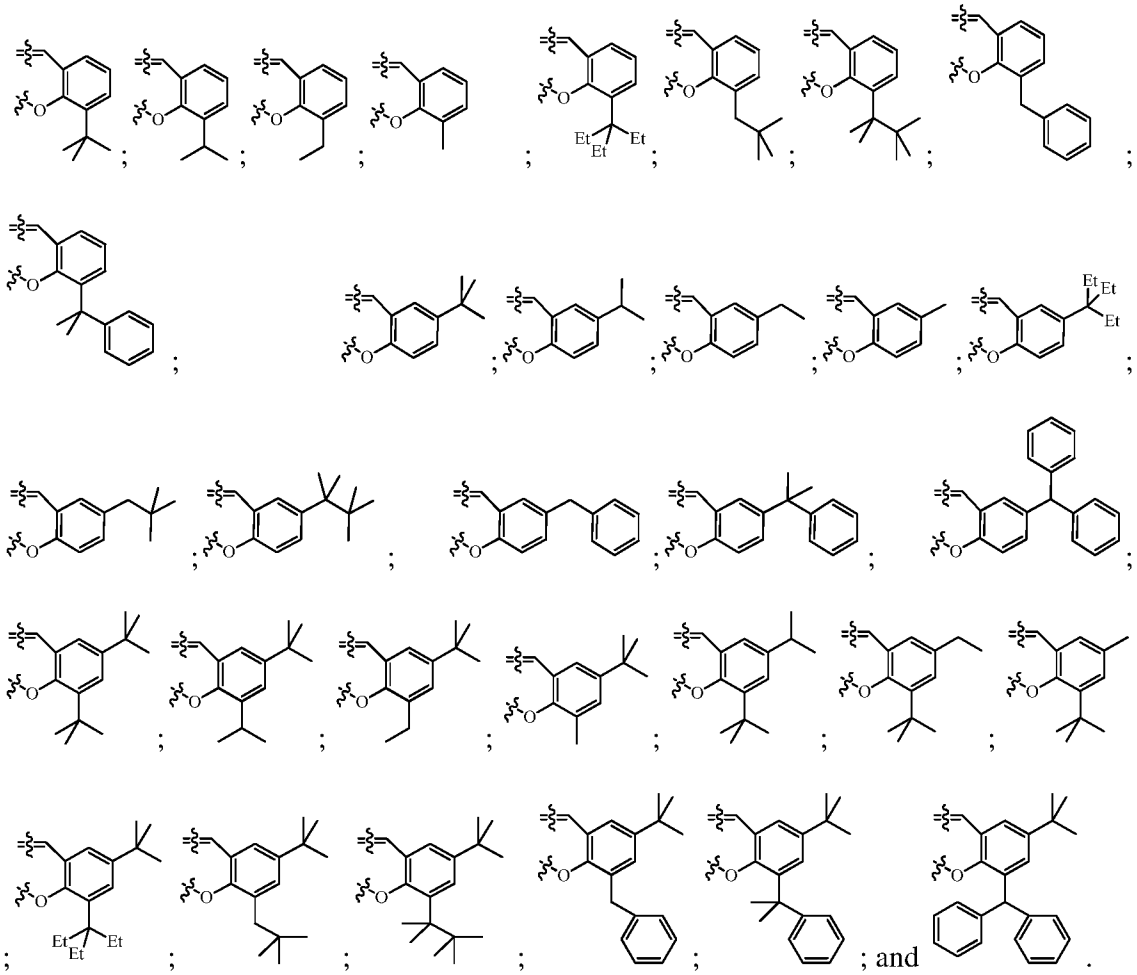
,

wherein each of M, R^d, and *a*, is as defined above and in the classes and subclasses herein,

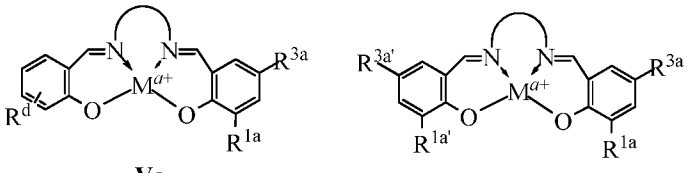
 represents is an optionally substituted moiety linking the two nitrogen atoms of the diamine portion of the salen ligand, where  is selected from the group consisting of a C_3-C_{14} carbocycle, a C_6-C_{10} aryl group, a C_3-C_{14} heterocycle, and a C_5-C_{10} heteroaryl group; or an optionally substituted C_{2-20} aliphatic group, wherein one or more

methylene units are optionally and independently replaced by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-OC(O)N(R^y)-$, $-N(R^y)C(O)O-$, -OC(O)O-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, $-SO_2-$, -C(=S)-, $-C(=NR^y)-$, $-C(=NOR^y)-$ or -N=N-.

[0172] In some embodiments metal complexes having formula **Ia** above, at least one of the phenyl rings comprising the salicylaldehyde-derived portion of the metal complex is independently selected from the group consisting of:



[0173] In some embodiments, a provided Lewis acid comprises a metallo salen compound, conforming to one of formulae **Va** or **Vb**:



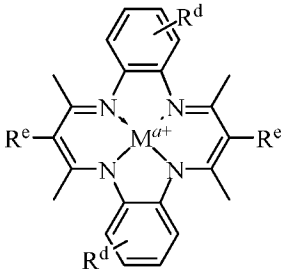
Va or **Vb**

where M, a, R^d, R^{1a}, R^{3a}, $R^{1a'}$, $R^{3a'}$, and , are as defined above and in the classes and subclasses herein.

[0174] In some embodiments of metal complexes having formulae **Va** or **Vb**, each R^{1a} and R^{3a} is, independently, optionally substituted C_1-C_{20} aliphatic.

[0175] In some embodiments, the moiety  comprises an optionally substituted 1,2-phenyl moiety.

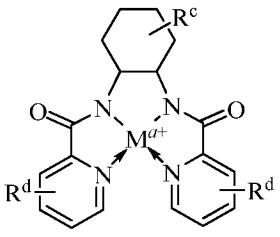
[0176] In some embodiments, Lewis acids included in carbonylation catalysts used in systems and methods described herein comprise metal- tmtaa complexes. In some embodiments, the moiety  has the structure:



where M, *a* and R^d are as defined above and in the classes and subclasses herein, and R^e at each occurrence is independently hydrogen, halogen, -OR, -NR^y_2, -SR^y, -CN, -NO_2, -SO_2R^y, -SOR^y, -$SO_2NR^y_2$; -CNO, -$NR^ySO_2R^y$, -NCO, -N_3, -SiR^y_3; or an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic having 1-4 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur; 6- to 10-membered aryl; 5- to 10-membered heteroaryl having 1-4 heteroatoms independently selected from nitrogen, oxygen, and sulfur; and 4- to 7-

membered heterocyclic having 1-2 heteroatoms independently selected from the group consisting of nitrogen, oxygen, and sulfur.

[0177] In some embodiments, the moiety  has the structure:



where each of M, *a*, R^c and R^d is as defined above and in the classes and subclasses herein.

[0178] In some embodiments, where carbonylation catalysts used in systems and methods described herein include a Lewis acidic metal complex, the metal atom is selected from the periodic table groups 2-13, inclusive. In some embodiments, M is a transition metal selected from the periodic table groups 4, 6, 11, 12 and 13. In some embodiments, M is aluminum, chromium, titanium, indium, gallium, zinc cobalt, or copper. In some embodiments, M is aluminum. In other embodiments, M is chromium.

[0179] In some embodiments, M has an oxidation state of +2. In some embodiments, M is Zn(II), Cu(II), Mn(II), Co(II), Ru(II), Fe(II), Co(II), Rh(II), Ni(II), Pd(II) or Mg(II). In some embodiments M is Zn(II). In some embodiments M is Cu(II).

[0180] In some embodiments, M has an oxidation state of +3. In some embodiments, M is Al(III), Cr(III), Fe(III), Co(III), Ti(III) In(III), Ga(III) or Mn(III). In some embodiments M is Al(III). In some embodiments M is Cr(III).

[0181] In some embodiments, M has an oxidation state of +4. In some embodiments, M is Ti(IV) or Cr(IV).

[0182] In some embodiments, M^1 and M^2 are each independently a metal atom selected from the periodic table groups 2-13, inclusive. In some embodiments, M is a transition metal

selected from the periodic table groups 4, 6, 11, 12 and 13. In some embodiments, M is aluminum, chromium, titanium, indium, gallium, zinc cobalt, or copper. In some embodiments, M is aluminum. In other embodiments, M is chromium. In some embodiments, M^1 and M^2 are the same. In some embodiments, M^1 and M^2 are the same metal, but have different oxidation states. In some embodiments, M^1 and M^2 are different metals.

[0183] In some embodiments, one or more of M^1 and M^2 has an oxidation state of +2. In some embodiments, M^1 is Zn(II), Cu(II), Mn(II), Co(II), Ru(II), Fe(II), Co(II), Rh(II), Ni(II), Pd(II) or Mg(II). In some embodiments M^1 is Zn(II). In some embodiments M^1 is Cu(II). In some embodiments, M^2 is Zn(II), Cu(II), Mn(II), Co(II), Ru(II), Fe(II), Co(II), Rh(II), Ni(II), Pd(II) or Mg(II). In some embodiments M^2 is Zn(II). In some embodiments M^2 is Cu(II).

[0184] In some embodiments, one or more of M^1 and M^2 has an oxidation state of +3. In some embodiments, M^1 is Al(III), Cr(III), Fe(III), Co(III), Ti(III) In(III), Ga(III) or Mn(III). In some embodiments M^1 is Al(III). In some embodiments M^1 is Cr(III). In some embodiments, M^2 is Al(III), Cr(III), Fe(III), Co(III), Ti(III) In(III), Ga(III) or Mn(III). In some embodiments M^2 is Al(III). In some embodiments M^2 is Cr(III).

[0185] In some embodiments, one or more of M^1 and M^2 has an oxidation state of +4. In some embodiments, M^1 is Ti(IV) or Cr(IV). In some embodiments, M^2 is Ti(IV) or Cr(IV).

[0186] In some embodiments, the metal-centered Lewis-acidic component of the carbonylation catalyst includes a dianionic tetradentate ligand. In some embodiments, the dianionic tetradentate ligand is selected from the group consisting of: porphyrin derivatives; salen derivatives; dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives; phthalocyaninate derivatives; and derivatives of the Trost ligand.

[0187] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum porphyrin compound. In some embodiments, the carbonylation

catalyst is $[(TPP)Al(THF)_2][Co(CO)_4]$ where TPP stands for tetraphenylporphyrin and THF stands for tetrahydrofuran.

[0188] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium porphyrin compound.

[0189] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salen compound. In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salophen compound.

[0190] In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum salen compound. In some embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum salophen compound.

[0191] In some embodiments, one or more neutral two electron donors coordinate to M M^1 or M^2 and fill the coordination valence of the metal atom. In some embodiments, the neutral two electron donor is a solvent molecule. In some embodiments, the neutral two electron donor is an ether. In some embodiments, the neutral two electron donor is tetrahydrofuran, diethyl ether, acetonitrile, carbon disulfide, or pyridine. In some embodiments, the neutral two electron donor is tetrahydrofuran . In some embodiments, the neutral two electron donor is an epoxide. In some embodiments, the neutral two electron donor is an ester or a lactone.

[0192] In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum porphyrin compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium porphyrin compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salen compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with a chromium salophen compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination

with an aluminum salen compound. In certain embodiments, the carbonylation catalyst includes a carbonyl cobaltate in combination with an aluminum salophen compound.

Biphasic Carbonylation Catalysts

[0193] In some embodiments, the carbonylation catalyst is biphasic. Thus, in certain variations, the carbonylation reaction product mixture comprises at least two phases, wherein one phase is a catalyst phase and a second phase is a product phase, wherein following the carbonylation reaction, the majority of the carbonylation catalyst is located in the catalyst phase, and the majority of the bPL produced is located in the product phase. For example, in some embodiments, between 50 wt % and 100 wt %, between 60 wt % and 100 wt %, between 70 wt % and 100 wt %, between 80 wt % and 100 wt %, between 90 wt % and 100 wt %, or between 95 wt % and 100 wt % of the carbonylation catalyst is located in the catalyst phase. In some embodiments, between 50 wt % and 100 wt %, between 60 wt % and 100 wt %, between 70 wt % and 100 wt %, between 80 wt % and 100 wt %, between 90 wt % and 100 wt %, or between 95 wt % and 100 wt % of the bPL produced is located in the product phase. In some embodiments, the biphasic carbonylation catalyst is any of the carbonylation catalysts described herein, provided the catalyst is at least partially immiscible with bPL. In other embodiments, the carbonylation catalyst is any of the carbonylation catalysts described herein modified to contain a substituent to make the modified catalyst at least partially immiscible with bPL.

[0194] In some embodiments, the carbonylation catalyst is at least partially immiscible with bPL under certain conditions, but miscible with bPL under other conditions. For example, in some variations, the biphasic catalyst is completely miscible with bPL in the carbonylation product stream at one temperature and at least partially immiscible with bPL in the carbonylation product stream at a lower temperature. In other variations, the biphasic catalyst comprises one or more ionizable functional groups which enable the catalyst to be miscible

with bPL in the carbonylation product stream at one pH, and at least partially immiscible at a different pH. Thus, in some embodiments, the biphasic catalyst is combined with EO and CO at a first pH to produce bPL, wherein the biphasic catalyst is miscible with bPL, and then the pH of the reaction mixture is changed such that the biphasic catalyst is at least partially immiscible with bPL.

Monitoring and Replacing Catalyst

[0195] In one aspect, the production system/production process is configured for continuous carbonylation of an epoxide or lactone feedstock, the process comprising the steps of:

reacting an epoxide or lactone feedstock with carbon monoxide in the presence of a catalyst comprising a Lewis acid and a metal carbonyl in a carbonylation reaction vessel;

measuring one or more parameters selected from the group consisting of:

i) a concentration of the Lewis acid, or a decomposition product thereof, within the carbonylation reaction vessel;

ii) a concentration of the Lewis acid, or a decomposition product thereof, in a product stream downstream from the carbonylation reaction vessel;

iii) a concentration of the metal carbonyl, or a decomposition product thereof, within the carbonylation reaction vessel;

iv) a concentration of the metal carbonyl, or a decomposition product thereof, in a product stream downstream from the carbonylation reaction vessel; and

v) a rate of the carbonylation reaction;

comparing the measured value of the one or more parameters to predetermined reference values for the one or more parameters; and

where the measured value of any one of parameters i), iii), or v) is less than the reference value, or where the measured value of any one of parameters ii) or iv) is greater than the

reference value, introducing to the carbonylation reaction vessel a catalyst replacement component which is different from the catalyst and comprises a species selected from the group consisting of the Lewis acid, a precursor to the Lewis acid, the metal carbonyl, and a precursor to the metal carbonyl.

[0196] In some embodiments, one of the one or more parameters measured is the concentration of the Lewis acid, or a decomposition product thereof, within the carbonylation reaction vessel. In some embodiments, the concentration of the Lewis acid within the carbonylation reaction vessel is measured. In some embodiments, the concentration of a decomposition product of the Lewis acid within the carbonylation reaction vessel is measured.

[0197] In some embodiments, one of the one or more parameters measured is the concentration of the metal carbonyl, or a decomposition product thereof, within the carbonylation reaction vessel. In some embodiments, the concentration of the metal carbonyl within the carbonylation reaction vessel is measured. In some embodiments, the concentration of a decomposition product of the metal carbonyl within the carbonylation reaction vessel is measured.

[0198] In some embodiments, one of the one or more parameters measured is the concentration of the Lewis acid, or a decomposition product thereof, in the product stream downstream from the carbonylation reaction vessel. In some embodiments, the concentration of the Lewis acid in the product stream downstream from the carbonylation reaction vessel is measured. In some embodiments, the concentration of a decomposition product of the Lewis acid in the product stream downstream from the carbonylation reaction vessel is measured.

[0199] In some embodiments, one of the one or more parameters measured is the concentration of the metal carbonyl, or a decomposition product thereof, in the product stream downstream from the carbonylation reaction vessel. In some embodiments, the concentration of the metal carbonyl in the product stream downstream from the carbonylation reaction vessel

is measured. In some embodiments, the concentration of a decomposition product of the metal carbonyl in the product stream downstream from the carbonylation reaction vessel is measured.

[0200] In some embodiments, one of the one or more parameters measured is the rate of the carbonylation reaction. In some embodiments, the rate of the carbonylation reaction is measured by the change in concentration of a carbonylation product in the carbonylation reaction vessel over time. In some embodiments, the rate of the carbonylation reaction is measured by the change in concentration of a carbonylation product in the product stream downstream from the carbonylation reaction vessel over time. In some embodiments, the carbonylation product is a beta-propiolactone. In some embodiments, the carbonylation product is beta-propiolactone (bPL). In some embodiments, the carbonylation product is a succinic anhydride. In some embodiments the carbonylation product is succinic anhydride (SA).

[0201] In some embodiments, the product stream is separated from the carbonylation reaction vessel by a nanofiltration membrane. In some embodiments, the nanofiltration membrane is selected based on its ability to retain solutes having a molecular weight greater than the molecular weight of the epoxide or lactone carbonylation products, but less than the molecular weights of either the Lewis acid or the metal carbonyl. In some embodiments, the nanofiltration membrane is designed to retain solutes having a molecular weight greater than the molecular weight of the epoxide or lactone carbonylation products, but less than the molecular weights of either the Lewis acid or the metal carbonyl.

[0202] In some embodiments, the catalyst replacement component comprises the Lewis acid, or a precursor to the Lewis acid. In some embodiments, the catalyst replacement component comprises the Lewis acid. In some embodiments, the catalyst replacement component comprises a precursor to the Lewis acid.

[0203] In some embodiments, the catalyst replacement component comprises the metal carbonyl, or a precursor to the metal carbonyl. In some embodiments, the catalyst replacement component comprises the metal carbonyl. In some embodiments, the catalyst replacement component comprises a precursor to the metal carbonyl.

[0204] In some embodiments, where more than one catalyst replacement component is added, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel separately. In some embodiments, where more than one catalyst replacement component is added, all of the one or more catalyst replacement components are added to the carbonylation reaction vessel together.

[0205] In some embodiments, each of the one or more catalyst replacement components is added individually to the carbonylation reaction vessel without solvent, as a solution in an organic solvent, or as a slurry. In some embodiments, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel without solvent. In some embodiments, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel as a solution in an organic solvent. In some embodiments, each of the one or more catalyst replacement components is added to the carbonylation reaction vessel as a slurry.

[0206] In certain embodiments, where more than one catalyst replacement component are added, each catalyst replacement component is dissolved in solution, and the solutions are combined enroute to the vessel, e.g., by using a mixing tee or flowing the combined solutions through a static mixer.

[0207] In certain embodiments, fresh catalyst may also be added to the reaction vessel at the same or different times as the one or more catalyst replacement components.

[0208] In certain embodiments, the catalyst replacement components are added under an atmosphere comprising CO. In certain embodiments, the CO is present at a pressure from

about 1 atmosphere to about 400 atmospheres. In certain embodiments, the catalyst replacement components are added under an atmosphere comprising CO at a pressure between about 1 atmosphere and about 100 atmospheres, or between about 1 atmosphere and about 50 atmospheres, or between about 10 atmospheres and about 20 atmospheres, or between about 5 atmospheres and about 10 atmospheres, or between about 1 atmosphere and about 5 atmospheres.

[0209] In some embodiments, the amount of a given catalyst replacement component added to the carbonylation reaction vessel is proportional to one of the parameters being measured in step (a). In some embodiments, the amount of a given catalyst replacement component is directly proportional to changes in the concentration of the parameter measured in the product stream downstream from the carbonylation reaction vessel.

[0210] In some embodiments, if the concentration of the Lewis acid, or a decomposition product thereof, measured in step (a) is increased in the product stream downstream from the carbonylation reaction vessel, an amount of Lewis acid that is proportional to the increase in the concentration of Lewis acid, or a decomposition product thereof, measured in step (a) is added to the carbonylation reaction vessel. In some embodiments, if the concentration of the Lewis acid, or a decomposition product thereof, measured in step (a) is decreased within the carbonylation reaction vessel, an amount of Lewis acid, or a precursor to the Lewis acid, that is proportional to the decrease in the concentration of Lewis acid, or a decomposition product thereof, measured in step (a) is added to the carbonylation reaction vessel. For example, if the concentration of the Lewis acid has decreased by 5%, an amount of the Lewis acid or precursor to the Lewis acid that is equivalent to about 5% of the amount of the Lewis acid initially charged into the carbonylation reaction vessel is added.

[0211] In some embodiments, if the rate of the carbonylation reaction, measured in step (a) is decreased, an amount of Lewis acid, or a precursor to the Lewis acid, that is proportional to the decrease in the rate of the carbonylation reaction is added to the carbonylation reaction vessel. In some embodiments, if the rate of the carbonylation reaction measured in step (a) is decreased, an amount of the metal carbonyl or a precursor to the metal carbonyl that is proportional to the decrease in the rate of the carbonylation reaction is added to the carbonylation reaction vessel. For example, if the rate of the carbonylation reaction has decreased by 5%, an amount of Lewis acid, precursor to the Lewis acid, metal carbonyl, or precursor to the metal carbonyl that is equivalent to about 5% of the amount of the Lewis acid or metal carbonyl initially charged into the carbonylation reaction vessel is added.

[0212] In some embodiments, if the concentration of the metal carbonyl, measured in step (a) is increased in the product stream downstream from the carbonylation reaction vessel, an amount of metal carbonyl, or a precursor to the metal carbonyl that is proportional to the increase in the amount of metal carbonyl measured in step (a) is added to the carbonylation reaction vessel. In some embodiments, if the concentration of the metal carbonyl, or a decomposition product thereof, measured in step (a) is decreased within the carbonylation reaction vessel, an amount of metal carbonyl, or a precursor to the metal carbonyl, that is proportional to the decrease in the amount of metal carbonyl, or a decomposition product thereof, measured in step (a) is added to the carbonylation reaction vessel. For example, if the concentration of the metal carbonyl has decreased by 5%, an amount of the metal carbonyl or precursor to the metal carbonyl that is equivalent to about 5% of the amount of the metal carbonyl initially charged into the carbonylation reaction vessel is added.

[0213] FIG. **14** includes carbonylation catalyst source 1403 that can feed fresh carbonylation catalyst in carbonylation catalyst stream 1407 to carbonylation reaction system inlet 1409. Carbonylation catalyst can arrive to the carbonylation catalyst source as either

solids (perhaps blanketed under CO or a suitable inert gas) or in solution of solvent such as hexane or THF. If solid catalysts, the solids can be unpacked and loaded into one or more hoppers under inert conditions (for example, CO or inert gas). The solids from the one or more hoppers can be metered into a suitable solvent before pumping. In some embodiments, the solid catalyst (or liquid catalyst) or catalyst precursors can be dispensed from a shipping vessel/container into an intermediate inert vessel to be mixed with solvent and then pumped. In some embodiments, the catalyst preparation system and connections are selected such that the catalyst/precursors are not exposed to the atmosphere. Carbonylation catalyst solutions can be suitable for direct pumping to the carbonylation reaction system. In some embodiments, the carbonylation catalyst feed is pumped under CO pressure to help ensure stability of the catalyst. Furthermore, carbonylation catalyst source and feed can be cooled below ambient temperature to ensure stability. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at between about 0.01 to 50 kg/hr, between about 0.01 to 40 kg/hr, between about 0.01 to 30 kg/hr, between about 0.01 to 20 kg/hr, between about 0.01 to 10 kg/hr, between about 0.2-5 kg/hr, between about 0.5-4 kg/hr, between about 1-3 kg/hr, between about 1-2 kg/hr, or about 1.4 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at between about 0.0001-10 kmol/hr, between about 0.0001-1 kmol/hr, between about 0.0001-0.1 kmol/hr, between about 0.0001-0.01 kmol/hr, between about 0.0005-0.001 kmol/hr, between about 0.0005-0.005 kmol/hr, or about 0.001 kmol/hr, or about 0.01 kmol/hr, or about 0.1 kmol/hr. In some embodiments, the carbonylation catalyst can be in a solvent such as THF so that the mass fraction of carbonylation catalyst in the stream from the carbonylation catalyst source can be between about 0.001-0.1, about 0.005-0.05, about 0.01-0.05, or about 0.02. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at a

temperature between about 10-30°C, between about 15-25°C, or about 20°C. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a carbonylation catalyst source at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Carbon Monoxide Source

[0214] Carbon monoxide is fed into the β-propiolactone production system/production process at an amount sufficient to carbonylate ethylene oxide to produce β-propiolactone. In some variations, this may be achieved performing the carbonylation reaction under a superatmospheric pressure of carbon monoxide. In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure in the range from about 50 psi (350 kPa) to about 5000 psi (35 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure from about 50 psi (350 kPa) to about 1000 psi (7 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure from about 50 psi (350 kPa) to about 500 psi (3.5 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure from about 100 psi (700 kPa) to about 400 psi (2.8 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process at a pressure of about 200 psi (1.4 MPa). In certain embodiments, the carbon monoxide is provided into the β-propiolactone production system/production process under an atmosphere having a partial pressure of CO of about 200 psi (1.4 MPa). The superatmospheric pressure of carbon monoxide may be provided in the form of pure carbon monoxide, or by providing a gas mixture containing carbon monoxide. In certain embodiments, the carbon monoxide may be provided in the form of substantially pure carbon monoxide. In other embodiments, the carbon monoxide may be provided in the form of

carbon monoxide mixed with one or more inert gases. In other embodiments, the carbon monoxide may be provided in the form of a mixture of carbon monoxide and hydrogen. In certain embodiments, the carbon monoxide may be provided in the form of a carbon monoxide-containing industrial process gas such as syngas, coal gas, wood gas, or the like.

[0215] FIG. **14** includes carbon monoxide source **1411** that can feed carbon monoxide to carbonylation reaction system inlet **1409**. In some embodiments, the carbon monoxide source that supplies carbon monoxide to the carbonylation reaction system can include fresh carbon monoxide source **1401** (i.e., main CO feed) and recycled carbon monoxide stream **1410** from the carbonylation reaction system. In some embodiments, the carbon monoxide source can be only the fresh carbon monoxide source. In some embodiments, the carbon monoxide source can be only the recycled carbon monoxide. In some embodiments, fresh carbon monoxide stream **1405** and/or the recycled carbon monoxide streams can be fed into carbon monoxide compressor **1401A** prior to the resultant stream from the carbon monoxide compressor (i.e., reactor carbon monoxide inlet stream) being fed into the carbonylation reaction system. In some embodiments, resultant stream from the carbon monoxide compressor **1411** (i.e., reaction system carbon monoxide inlet stream) can be the carbon monoxide source. The carbon monoxide source can be compressed to the pressure at or above the carbonylation reaction system pressure and then fed to the carbonylation system. In some embodiments, the fresh carbon monoxide source (i.e., main CO feed) and the recycled carbon monoxide can be compressed in separate compressors. One reason recycled carbon monoxide can be compressed separately from the fresh carbon monoxide feed (i.e., main CO feed) to reaction system pressure is to avoid contamination of the main compressor (i.e., fresh feed compressor) with hazardous components such as ethylene oxide and bPL that may be present in the carbon monoxide recycle stream. Some of these potentially hazardous components may be removed from the compressor as partially liquefied components as waste. In some embodiments, these

potentially hazardous components can also be recycled to the carbonylation reaction system. In some embodiments, the compressed carbon monoxide from both compressors can be fed to the carbonylation reaction system as the reaction system carbon monoxide inlet stream.

[0216] In some embodiments, the fresh carbon monoxide source can provide at least about 1000 kg/hr CO, at least about 1200 kg/hr CO, at least about 1400 kg/hr CO, at least about 1500 kg/hr CO, at least about 1600 kg/hr CO, at least about 2000 kg/hr CO, at least about 4000 kg/hr CO, at least about 5000 kg/hr CO, at least about 10000 kg/hr CO, at least about 12000 kg/hr CO, at least about 14000 kg/hr CO, at least about 15000 kg/hr CO, or at least about 16000 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide at least about 30 kmol/hr CO, at least about 40 kmol/hr CO, at least about 50 kmol/hr CO, at least about 55 kmol/hr CO, or at least about 60 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide about 1000 kg/hr CO to about 16000 kg/hr CO, about 1200 kg/hr CO to about 16000 kg/hr CO, about 1400 kg/hr CO to about 16000 kg/hr CO, about 1500 kg/hr CO to about 16000 kg/hr CO, about 1600 kg/hr CO to about 16000 kg/hr CO, about 2000 kg/hr CO to about 16000 kg/hr CO, about 4000 kg/hr CO to about 16000 kg/hr CO, about 6000 kg/hr CO to about 16000 kg/hr CO, about 1000 kg/hr CO to about 16000 kg/hr CO, or about 1400 kg/hr CO to about 16000 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide about 1000 kg/hr CO, about 1200 kg/hr CO, about 1400 kg/hr CO, about 1500 kg/hr CO, about 1600 kg/hr CO, about 1800 kg/hr CO, about 2000 kg/hr CO, about 2400 kg/hr CO, about 2600 kg/hr CO, about 2800 kg/hr CO, about 3000 kg/hr CO, about 3200 kg/hr CO, about 4000 kg/hr CO, about 6000 kg/hr CO, about 8000 kg/hr CO, about 10000 kg/hr CO, about 12000 kg/hr CO, about 14000 kg/hr CO, or about 16000 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide at least about 30 kmol/hr CO, at least about 40 kmol/hr CO, at least about 50 kmol/hr CO, at least about 55 kmol/hr CO, at least about 60 kmol/hr CO, at least about 100 kmol/hr CO, at least about 150 kmol/hr CO, at least

about 200 kmol/hr CO, at least about 250 kmol/hr CO, at least about 300 kg/hr CO, at least about 350 kmol/hr CO, at least about 400 kmol/hr CO, at least about 500 kmol/hr CO, at least about 550 kmol/hr CO, or at least about 600 kg/hr CO. In some embodiments, the fresh carbon monoxide source can provide about 30 kmol/hr CO to about 60 kmol/hr CO, about 40 kmol/hr CO to about 60 kmol/hr CO, about 50 kmol/hr CO to about 60 kmol/hr CO, about 30 kmol/hr CO to about 600 kmol/hr CO, about 40 kmol/hr CO to about 600 kmol/hr CO, about 50 kmol/hr CO to about 600 kmol/hr CO, about 55 kmol/hr CO to about 600 kmol/hr CO, about 100 kmol/hr CO to about 600 kmol/hr CO, about 200 kg/hr CO to about 600 kmol/hr CO, about 300 kmol/hr CO to about 600 kmol/hr CO, about 400 kmol/hr CO to about 600 kmol/hr CO, about 500 kmol/hr CO to about 600 kmol/hr CO, about 525 kmol/hr CO to about 600 kmol/hr CO, about 550 kg/hr CO to about 600 kmol/hr CO. In some embodiments, the fresh carbon monoxide from the fresh carbon monoxide source may have some impurities and thus may require additional purification steps such as adsorption. In some embodiments, the flow rate from the fresh carbon monoxide source is set to about the stoichiometric value for the carbonylation reaction, to about 5% higher than the stoichiometric value, to about 10% higher than the stoichiometric value, to about 15% higher than the stoichiometric value, or to about 20% higher than the stoichiometric value.

[0217] In some embodiments, the recycled carbon monoxide from the carbonylation reaction system can provide at least about 100 kg/hr CO, at least about 150 kg/hr CO, at least about 200 kg/hr CO, at least about 255 kg/hr CO, at least about 300 kg/hr CO, at least about 350 kg/hr CO, at least about 500 kg/hr CO, at least about 600 kg/hr CO, at least about 800 kg/hr CO, at least about 1000 kg/hr CO, at least about 1250 kg/hr CO, at least about 1500 kg/hr CO, at least about 1750 kg/hr CO, at least about 2000 kg/hr CO, at least about 2500 kg/hr CO, at least about 3000 kg/hr CO, or at least about 3500 kg/hr CO. In some embodiments, the recycled carbon monoxide from the carbonylation reaction system can provide from about 100

kg/hr CO to about 350 kg/hr CO, about 150 kg/hr CO to about 350 kg/hr CO, about 200 kg/hr CO to about 350 kg/hr CO, about 255 kg/hr CO to about 350 kg/hr CO, about 300 kg/hr CO to about 350 kg/hr CO, from about 100 kg/hr CO to about 3500 kg/hr CO, about 150 kg/hr CO to about 3500 kg/hr CO, about 200 kg/hr CO to about 3500 kg/hr CO, about 255 kg/hr CO to about 3500 kg/hr CO, about 300 kg/hr CO to about 3500 kg/hr CO, about 350 kg/hr CO to about 3500 kg/hr CO, about 1000 kg/hr CO to about 3500 kg/hr CO, about 1500 kg/hr CO to about 3500 kg/hr CO, about 2000 kg/hr CO to about 3500 kg/hr CO, about 2550 kg/hr CO to about 3500 kg/hr CO, about 3000 kg/hr CO to about 3500 kg/hr CO. In some embodiments, the recycled carbon monoxide from the carbonylation reaction system can provide about 100 kg/hr CO, about 150 kg/hr CO, about 200 kg/hr CO, about 255 kg/hr CO, about 300 kg/hr CO, about 350 kg/hr CO, about 500 kg/hr CO, about 750 kg/hr CO, about 1000 kg/hr CO, about 1250 kg/hr CO, about 1500 kg/hr CO, about 2000 kg/hr CO, about 2500 kg/hr CO, about 3000 kg/hr CO, or about 3500 kg/hr CO. In some embodiments, the recycled carbon monoxide source can provide at least about 3 kmol/hr CO, at least about 5 kmol/hr CO, at least about 7 kmol/hr CO, at least about 9 kmol/hr CO, at least about 10 kmol/hr CO, at least about 15 kmol /hr CO, at least 50 kmol /hr CO, at least 100 kmol /hr CO, or at least 150 kmol /hr CO. In some embodiments, the mass fraction of CO in the recycled carbon monoxide stream can be at least about 0.70, at least about 0.75, at least about 0.8, or at least about 0.85. In some embodiments, the mole fraction of CO in the recycled carbon monoxide stream can be at least about 0.70, at least about 0.75, at least about 0.8, at least about 0.85, at least about 0.896, at least about 0.9, or at least about 0.95. In some embodiments, the mole fraction of CO in the recycled carbon monoxide stream can be 0.70 to 1.0, 0.75 to 1.0, 0.8 to 1.0, 0.85 to 1.0, 0.896 to 1.0, 0.9 to 1.0, or 0.95 to 1.0. The recycled carbon monoxide stream from the carbonylation reaction system can also include unreacted ethylene oxide (in about at most 10 kg/hr, at most 15 kg/hr, at most 20 kg/hr, at most 25 kg/hr, at most 50 kg/hr, at most 75 kg/hr, at most 100 kg/hr, at most 150

kg/hr, at most 200 kg/hr, or at most 250 kg/hr or a mass fraction of between about 0.05-0.075, about 0.055-0.07, about 0.06-0.07, about at most 0.065, about at most 0.07, or about at most 0.075), secondary reaction product acetaldehyde (in about at most 0.5 kg/hr, at most about 1 kg/hr, at most about 1.3 kg/hr, at most about 2 kg/hr, at most about 4 kg/hr, at most about 6 kg/hr, at most about 10 kg/hr, at most about 13 kg/hr or a mass fraction of about 0.001-0.009, about 0.003-0.005, or about most 0.004, about at most 0.005, or at most about 0.009), bPL (in about at most about 0.005 kg/hr, at most about 0.01 kg/hr, at most about 0.015 kg/hr, about at most about 0.019 kg/hr, at most about 0.05 kg/hr, at most about 0.1 kg/hr, at most about 0.15 kg/hr, or about at most about 0.19 kg/hr), and the remainder solvent (e.g., THF).

[0218] In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at least about 1000 kg/hr, at least about 1250 kg/hr, at least about 1500 kg/hr, at least about 1600 kg/hr, at least about 1655 kg/hr, at least about 1700 kg/hr, at least about 4000 kg/hr, at least about 5000 kg/hr, at least about 700 kg/hr, at least about 8500 kg/hr, at least about 10000 kg/hr, at least about 12500 kg/hr, at least about 15000 kg/hr, at least about 16000 kg/hr, at least about 16550 kg/hr, or at least about 17000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at about 1000 kg/hr to about 1700 kg/hr, about 1250 kg/hr to about 1700 kg/hr, about 1500 kg/hr to about 1700 kg/hr, about 1600 kg/hr to about 1700 kg/hr, about 1655 kg/hr to about 1700 kg/hr, 1000 kg/hr to about 17000 kg/hr, about 1250 kg/hr to about 17000 kg/hr, about 1500 kg/hr to about 17000 kg/hr, about 1600 kg/hr to about 17000 kg/hr, about 1655 kg/hr to about 17000 kg/hr, about 1700 kg/hr to about 17000 kg/hr, at about 2000 kg/hr to about 17000 kg/hr, about 3000 kg/hr to about 17000 kg/hr, about 4000 kg/hr to about 17000 kg/hr, about 6000 kg/hr to about 17000 kg/hr, about 8000 kg/hr to about 17000 kg/hr, about 1200 kg/hr to about 17000 kg/hr, about 1400 kg/hr to about 17000 kg/hr, about 1500 kg/hr to about 17000 kg/hr, or about 1600 kg/hr to about 17000 kg/hr. In some

embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at about 1000 kg/hr, about 1250 kg/hr, about 1500 kg/hr, about 1600 kg/hr, about 1655 kg/hr, about 1700 kg/hr, about 2000 kg/hr, about 1900 kg/hr, about 2500 kg/hr, about 3000 kg/hr, about 4000 kg/hr, about 6000 kg/hr, about 8000 kg/hr, about 10000 kg/hr, about 12000 kg/hr, about 13000 kg/hr, about 14000 kg/hr, about 15000 kg/hr, about 16000 kg/hr, or about 17000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at least about 35 kmol/hr, at least about 45 kmol/hr, at least about 50 kmol/hr, at least about 55 kmol/hr, or at least about 59 kmol/hr. As previously discussed, in some embodiments, the carbon monoxide source can include some recycled carbon monoxide from the carbonylation reaction system. Accordingly, in some embodiments, the inlet to the carbonylation reaction system can also receive ethylene oxide (in about 5-300 kg/hr, about 10-200 kg/hr, about 10-100 kg/hr, about 10-50 kg/hr, about 10-30 kg/hr, about 10-20 kg/hr, or at most about 15 kg/hr, at most about 50 kg/hr, at most about 100 kg/hr, at most about 150 kg/hr, at most about 200 kg/hr, at most about 300 kg/hr, or a mass fraction of about 0.001-0.05, about 0.005-0.02, or at most about 0.009, at most about 0.02, or at most about 0.05), acetaldehyde (in about 0.25-15 kg/hr, about 0.5-12.5 kg/hr, about 0.25-10 kg/hr, about 0.5-5 kg/hr, about 0.25-1.5 kg/hr, about 0.5-1.25 kg/hr, or at most about 0.9 kg/hr, at most about 1.5 kg/hr, at most about 3 kg/hr, at most about 6 kg/hr, at most about 12 kg/hr, at most about 15 kg/hr, or a mass fraction of about 0.001-0.05, about 0.005-0.02, or at most about 0.009, at most about 0.02, or at most about 0.05), and the remainder solvent from the carbon monoxide source. In some embodiments, the mass fraction of CO from the carbon monoxide source can be at least about 0.9, at least about 0.95, at least about 0.985, or at least about 0.99. In some embodiments, the mole fraction of CO from the carbon monoxide source can be at least about 0.9, at least about 0.95, at least about 0.98, at least about 0.99, or at least about 0.995. In some embodiments, the mole fraction of CO from

the carbon monoxide source can be 0.9 to 1.0, 0.95 to 1.0, 0.98 to 1.0, 0.99 to 1.0, or 0.995 to 1.0.

[0219] In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at a temperature between about 10-170°C, between about 30-70°C, between about 40-60°C, between about 45-55°C, or about 50°C. In some embodiments, the inlet to the carbonylation reaction system can receive carbon monoxide from a carbon monoxide source at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Solvent Source

[0220] The solvent may be selected from any solvents described herein, and mixtures of such solvents. In some variations, the solvent is an organic solvent. In certain variations, the solvent is an aprotic solvent.

[0221] In some embodiments, the solvent includes dimethylformamide, N-methyl pyrrolidone, tetrahydrofuran, toluene, xylene, diethyl ether, methyl-tert-butyl ether, acetone, methylethyl ketone, methyl-iso-butyl ketone, butyl acetate, ethyl acetate, dichloromethane, and hexane, and mixtures of any two or more of these. In general polar aprotic solvents or hydrocarbons are suitable for this step.

[0222] Additionally, in one variation, β-lactone may be utilized as a co-solvent. In other variations, the solvent may include ethers, hydrocarbons and non protic polar solvents. In some embodiments, the solvent includes tetrahydrofuran ("THF"), sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, dimethoxy ethane, acetone, and methylethyl ketone. In other embodiments, the solvent includes tetrahydrofuran, tetrahydropyran, 2,5-dimethyl

tetrahydrofuran, sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, propyl acetate, butyl acetate, 2-butanone, cyclohexanone, toluene, difluorobenzene, dimethoxy ethane, acetone, and methylethyl ketone. In certain variations, the solvent is a polar donating solvent. In one variation, the solvent is THF.

[0223] In some embodiments, the catalyst and/or solvent stream is recycled to the feed stream or to the carbonylation reaction system. In some embodiments, the portion of the solvent and/or catalyst from the reaction product stream recycled to the carbonylation reactor or feed stream ranges from about 0% to about 100%. In some embodiments, the portion of the solvent and/or catalyst from the reaction product stream recycled to the carbonylation reactor or feed stream is about 100%, about 90%, about 80%, about 70%, about 60%, about 50%, about 40%, about 30%, about 20%, about 10%, or about 0%. In some embodiments, a different percentage of the catalyst, as compared to the solvent is recycled, i.e., the proportions of either the catalyst or solvent component do not need to be equal.

[0224] Referring again to the exemplary system depicted in FIG. **14**, in some embodiments, solvent feed 1424 can supply solvent to the carbonylation reaction system inlet 1409. Solvent can be fed to the carbonylation reaction system suing a pump. In addition, the solvent streams, sources, storage tanks, etc, can be maintained under an inert or CO atmosphere. In some embodiments, the solvent feed that supplies solvent to the carbonylation reaction system can include solvent 1408 from fresh solvent source 1404, recycled solvent 1423 from the BPL purification system, and/or solvent in recycled carbonylation catalyst stream 1412 from the carbonylation catalyst isolation system. In some embodiments, the recycled solvent from the BPL purification system can be stored in a make-up solvent reservoir. In some embodiments,

the solvent feed that supplies solvent to the carbonylation reaction system can include solvent from the make-up solvent reservoir. In some embodiments, solvent can be purged from the system. In some embodiments, the purged solvent can be solvent from the recycled solvent of the BPL purification system. In some embodiments, solvent from the fresh solvent source is also stored into the make-up solvent reservoir to dilute the recycled solvent from the BPL purification system with fresh solvent. In some embodiments, fresh solvent is fed from the fresh solvent source to the make-up solvent reservoir prior to entering the carbonylation reaction system. In some embodiments, solvent from the fresh solvent source, the BPL purification system, and the carbonylation catalyst isolation system can be purified by operations such as adsorption to remove oxygen and water that can inhibit the carbonylation catalyst. In some embodiments, the amount of oxygen and/or water in all streams entering the carbonylation reaction system is less than about 500 ppm, less than about 250 ppm, less than about 100 ppm, less than about 50 ppm, less than about 20 ppm, less than about 10 ppm, less than about 5 ppm, less than about 2 ppm, or less than about 1 ppm.

[0225] In some embodiments, the fresh solvent source can provide at least about 50 kg/hr solvent, at least about 100 kg/hr solvent, at least about 150 kg/hr solvent, at least about 188 kg/hr solvent, at least about 200 kg/hr solvent, at least about 250 kg/hr solvent, at least about 500 kg/hr solvent, at least about 1000 kg/hr solvent, at least about 1500 kg/hr solvent, at least about 1880 kg/hr solvent, at least about 2000 kg/hr solvent, or at least about 2500 kg/hr solvent. In some embodiments, the fresh solvent source can provide about 50 kg/hr to about 250 kg/hr solvent, about 100 kg/hr to about 250 kg/hr solvent, about 150 kg/hr to about 250 kg/hr solvent, about 188 kg/hr to about 250 kg/hr solvent, about 200 kg/hr to about 250 kg/hr solvent, about 50 kg/hr to about 2500 kg/hr solvent, about 100 kg/hr to about 2500 kg/hr solvent, about 150 kg/hr to about 2500 kg/hr solvent, about 188 kg/hr to about 2500 kg/hr solvent, about 200 kg/hr to about 2500 kg/hr solvent, about 250 kg/hr to about 2500 kg/hr solvent, about 500 kg/hr to

about 2500 kg/hr solvent, about 1000 kg/hr to about 2500 kg/hr solvent, about 1500 kg/hr to about 2500 kg/hr solvent, about 1880 kg/hr to about 2500 kg/hr solvent, about 2000 kg/hr to about 2500 kg/hr solvent, or about 2250 kg/hr to about 2500 kg/hr solvent. In some embodiments, the fresh solvent source can provide about 50 kg/hr solvent, about 100 kg/hr solvent, about 150 kg/hr solvent, about 188 kg/hr solvent, about 200 kg/hr solvent, about 250 kg/hr solvent, about 500 kg/hr solvent, about 1000 kg/hr solvent, about 1500 kg/hr solvent, about 1880 kg/hr solvent, about 2000 kg/hr solvent, or about 2500 kg/hr solvent. In some embodiments, the fresh solvent source can provide at least about 1 kmol/hr solvent, at least about 2 kmol/hr solvent, at least about 2.6 kmol/hr solvent, at least about 3 kmol/hr solvent, at least about 50 kmol/hr solvent, at least about 100 kmol/hr solvent, at least about 150 kmol/hr solvent, at least about 250 kmol/hr solvent, at least about 400 kmol/hr solvent, or at least about 500 kmol/hr solvent.

[0226] In some embodiments, the recycled solvent from the BPL purification system can provide at least about 8000 kg/hr solvent, at least about 9000 kg/hr solvent, at least about 10000 kg/hr solvent, at least about 10444 kg/hr solvent, at least about 12000 kg/hr solvent, at least about 80000 kg/hr solvent, at least about 90000 kg/hr solvent, at least about 100000 kg/hr solvent, at least about 104440 kg/hr solvent, or at least about 120000 kg/hr solvent. In some embodiments, the recycled solvent from the BPL purification system can provide between about 8000 kg/hr to about 12000 kg/hr solvent, between about 9000 kg/hr to about 12000 kg/hr solvent, between about 10000 kg/hr to about 12000 kg/hr solvent, between about 10444 kg/hr to about 12000 kg/hr solvent, about 8000 kg/hr to about 120000 kg/hr solvent, between about 9000 kg/hr to about 120000 kg/hr solvent, between about 10000 kg/hr to about 120000 kg/hr solvent, between about 10444 kg/hr to about 120000 kg/hr solvent, between about 12000 kg/hr to about 120000 kg/hr solvent, about 40000 kg/hr to about 120000 kg/hr solvent, about 60000 kg/hr to about 120000 kg/hr solvent, about 80000 kg/hr to about 120000 kg/hr solvent, between

about 90000 kg/hr to about 120000 kg/hr solvent, between about 100000 kg/hr to about 120000 kg/hr solvent, between about 104440 kg/hr to about 120000 kg/hr solvent, or between about 120000 kg/hr to about 120000 kg/hr solvent. In some embodiments, the recycled solvent from the BPL purification system can provide about 8000 kg/hr solvent, about 9000 kg/hr solvent, about 10000 kg/hr solvent, about 10444 kg/hr solvent, or about 12000 kg/hr solvent. In some embodiments, the recycled solvent from the BPL purification system can provide at least about 100 kmol/hr solvent, at least about 120 kmol/hr solvent, at least about 140 kmol/hr solvent, at least about 145 kmol/hr solvent, at least about 150 kmol/hr solvent, at least 250 kmol/hr solvent, at least 350 kmol/hr solvent, or at least 500 kmol/hr solvent. In some embodiments, the mass fraction of solvent in the recycled solvent stream can be at least about 0.85, at least about 0.90, at least about 0.95, or at least about 0.995. In some embodiments, the mole fraction of solvent in the recycled solvent stream can be at least about 0.85, at least about 0.90, at least about 0.95, at least about 0.98, at least about 0.99, or at least about 0.993. In some embodiments, the mole fraction of solvent in the recycled solvent stream can be 0.85 to 1.0, 0.90 to 1.0, 0.95 to 1.0, 0.98 to 1.0, 0.99 to 1.0, or 0.993 to 1.0. In some embodiments, the mole fraction of solvent in the recycled solvent stream can be about 0.85, about 0.90, about 0.95, about 0.98, about 0.99, or about 0.993. The recycled solvent stream from the BPL purification system can also include unreacted carbon monoxide (in about at most 0.001 kg/hr, at most about 0.0025 kg/hr, at most about 0.005 kg/hr, at most about 0.01 kg/hr, at most 0.02 kg/hr, at most about 0.025 kg/hr, at most about 0.05 kg/hr, or at most about 0.01 kg/hr or between 0 and 0.005 kg/hr, or between 0 and 0.05 kg/hr) unreacted ethylene oxide (in about at most about 10 kg/hr, at most about 20 kg/hr, at most about 30 kg/hr, at most about 33 kg/hr, at most about 50 kg/hr, at most about 100 kg/hr, at most about 200 kg/hr, or at most about 330 kg/hr, or a mass fraction of between about 0.001-0.005, about 0.02-0.004, or at most about 0.003, at most about 0.004, or at most about 0.005), secondary reaction product acetaldehyde

(in about at most 3 kg/hr, at most about 5 kg/hr, at most about 8.2 kg/hr, at most about 10 kg/hr, at most about 15 kg/hr, at most 30 kg/hr, at most about 50 kg/hr, or at most about 82 kg/hr or a mass fraction of at most about 0.001, or between 0 and 8.2 kg/hr), and bPL (in at most about 2 kg/hr, at most about 3 kg/hr, at most about 5 kg/hr, at most about 7 kg/hr, at most about 10 kg/hr, at most about 25 kg/hr, at most about 50 kg/hr, or at most about 70 kg/hr or a mass fraction of at most about 0.001, or between 0 and 7 kg/hr, or between 0 and 70 kg/hr).

[0227] In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 1000 kg/hr solvent, at least about 1500 kg/hr solvent, at least about 1700 kg/hr solvent, at least about 1840 kg/hr solvent, at least about 2000 kg/hr solvent, at least about 5000 kg/hr solvent, at least about 10000 kg/hr solvent, at least about 15000 kg/hr solvent, at least about 17000 kg/hr solvent, at least about 18400 kg/hr solvent, or at least about 20000 kg/hr solvent. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide about 1000 kg/hr to about 2000 kg/hr solvent, about 1500 kg/hr to about 2000 kg/hr solvent, about 1700 kg/hr to about 2000 kg/hr solvent, about 1840 kg/hr to about 2000 kg/hr solvent, about 1000 kg/hr to about 20000 kg/hr solvent, about 1500 kg/hr to about 20000 kg/hr solvent, about 1700 kg/hr to about 20000 kg/hr solvent, about 1840 kg/hr to about 20000 kg/hr solvent, about 2000 kg/hr to about 20000 kg/hr solvent, about 5000 kg/hr to about 20000 kg/hr solvent, about 7500 kg/hr to about 20000 kg/hr solvent, about 12500 kg/hr to about 20000 kg/hr solvent, about 15000 kg/hr to about 20000 kg/hr solvent, or about 17500 kg/hr to about 20000 kg/hr solvent. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide about 1000 kg/hr solvent, about 1500 kg/hr solvent, about 1700 kg/hr solvent, about 1840 kg/hr solvent, about 2000 kg/hr solvent, about 2500 kg/hr solvent, about 3000 kg/hr solvent, about 5000 kg/hr solvent, about 7000 kg/hr solvent, about 10000 kg/hr solvent, about 12500 kg/hr solvent, about 15000 kg/hr solvent, or

about 20000 kg/hr solvent. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 10 kmol/hr solvent, at least about 15 kmol/hr solvent, at least about 20 kmol/hr solvent, at least about 25 kmol/hr solvent, at least about 30 kmol/hr solvent, at least about 50 kmol/hr solvent, at least about 75 kmol/hr solvent, at least about 100 kmol/hr solvent, at least about 150 kmol/hr solvent, at least about 175 kmol/hr solvent, at least about 200 kmol/hr solvent, at least about 250 kmol/hr solvent, or at least about 300 kmol/hr solvent In some embodiments, the mass fraction of solvent in the recycled carbonylation catalyst stream can be at least about 0.60, at least about 0.65, at least about 070, or at least about 0.74. In some embodiments, the mole fraction of solvent in the recycled carbonylation catalyst stream can be at least about 0.60, at least about 0.65, at least about 0.70, at least about 0.75, at least about 0.80, or at least about 0.85. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can also include unreacted carbon monoxide (in about at most 0.5 kg/hr, at most about 1 kg/hr, at most about 1.2 kg/hr, at most about 1.5 kg/hr, at most 5 kg/hr, at most about 10 kg/hr, at most about 12 kg/hr, or at most about 15 kg/hr, or a mass fraction of at most about 0.001), unreacted ethylene oxide (in about at most about 10 kg/hr, at most about 20 kg/hr, at most 30 kg/hr, at most 33 kg/hr, at most about 100 kg/hr, at most about 200 kg/hr, at most 300 kg/hr, or at most 330 kg/hr or a mass fraction of between about 0.005-0.01, about 0.01-0.05, or at most about 0.014, or at most about 0.10), secondary reaction product acetaldehyde (in about at most 1 kg/hr, at most about 2 kg/hr, at most about 3.3 kg/hr, at most 10 kg/hr, at most about 20 kg/hr, or at most about 33 kg/hr or a mass fraction of at most about 0.01), secondary reaction product succinic anhydride (in about at most 1 kg/hr, at most about 2 kg/hr, at most about 3 kg/hr, at most 10 kg/hr, at most about 20 kg/hr, or at most about 30 kg/hr or a mass fraction of at most about 0.01), bPL (in about at most about 250 kg/hr, at most about 400 kg/hr, at most about 500 kg/hr, at most about 545 kg/hr, at most about 1000 kg/hr, at most

about 2500 kg/hr, at most about 4000 kg/hr, or at most about 5450 kg/hr or a mass fraction of at most about 0.1, at most about 0.15, at most about 0.2, at most about 0.22, or at most about 0.23), and carbonylation catalyst or components thereof.

[0228] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0229] In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 25 kg/hr carbonylation catalyst, at least about 35 kg/hr carbonylation catalyst, at least about 45 kg/hr carbonylation catalyst, at least about 50 kg/hr carbonylation catalyst, at least about 53 kg/hr carbonylation catalyst, at least about 100 kg/hr carbonylation catalyst, at least about 250 kg/hr carbonylation catalyst, at least about 350 kg/hr carbonylation catalyst, at least about 450 kg/hr carbonylation catalyst, at least about 500 kg/hr carbonylation catalyst, at least about 530 kg/hr carbonylation catalyst. In some embodiments, the recycled carbonylation catalyst stream from the carbonylation catalyst isolation system can provide at least about 0.01 kmol/hr carbonylation catalyst, at least about 0.025 kmol/hr carbonylation catalyst, at least about 0.04 kmol/hr carbonylation catalyst, at least about 0.05 kmol/hr carbonylation catalyst, at least about 0.056 kmol/hr carbonylation catalyst, at least about 0.1 kmol/hr carbonylation catalyst, at least about 0.25 kmol/hr carbonylation catalyst, at least about 0.4 kmol/hr carbonylation catalyst, at least about 0.5 kmol/hr carbonylation catalyst, or at least about 0.56 kmol/hr carbonylation catalyst. In some embodiments, the mass fraction of carbonylation catalyst in the recycled carbonylation

catalyst stream can be at least about 0.002, at least about 0.015, at least about 0.02, or at least about 0.022. In some embodiments, the mole fraction of carbonylation catalyst in the recycled carbonylation catalyst stream can be at least about 0.0002, at least about 0.0015, at least about 0.002, at least about 0.003, at least about 0.004, or at least about 0.005.

[0230] In some embodiments, the inlet to the carbonylation reaction system can receive solvent from solvent feed 1424 at least about 10000 kg/hr, at least about 11000 kg/hr, at least about 12000 kg/hr, at least about 12250 kg/hr, at least about 13000 kg/hr, at least about 25000 kg/hr, at least about 50000 kg/hr, at least about 100000 kg/hr, at least about 110000 kg/hr, at least about 120000 kg/hr, at least about 122500 kg/hr, or at least about 130000 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive solvent from a solvent feed at least about 150 kmol/hr, at least about 160 kmol/hr, at least about 170 kmol/hr, at least about 180 kmol/hr, at least about 190 kmol/hr, at least about 500 kmol/hr, at least about 1000 kmol/hr, at least about 1500 kmol/hr, at least about 1600 kmol/hr, at least about 1700 kmol/hr, at least about 1800 kmol/hr, or at least about 1900 kmol/hr In some embodiments, the amount of solvent in the solvent feed to the carbonylation reaction system can be fixed to ensure the residence time in the carbonylation reaction system is at a set time. For example, the residence time can be about 1-500 minutes, about 20-450 minutes, about 30-300 minutes, about 35-200 minutes, or about 40-80 minutes. As previously discussed, in some embodiments, the solvent introduced to the carbonylation reaction system can include some recycled solvents from the carbonylation catalyst isolation system and the BPL purification system. Accordingly, in some embodiments, the inlet to the carbonylation reaction system can also receive carbon monoxide (in about 0.1-10 kg/hr, about 0.5-5 kg/hr, about 0.1-10 kg/hr, about 0.1-50 kg/hr, about 0.1-100 kg/hr, about 0.5-50 kg/hr, at most about 50 kg/hr, at most about 10 kg/hr, at most about 5 kg/hr, at most about 3 kg/hr, or at most about 1.3 kg/hr), ethylene oxide (in about 40-80 kg/hr, about 50-70 kg/hr, about 40-150 kg/hr, about 40-250 kg/hr, about 50-500 kg/hr, about 50-800 kg/hr,

at most about 800 kg/hr, at most about 500 kg/hr, about most about 250 kg/hr, 80 kg/hr, at most about 70 kg/hr, or at most about 66 kg/hr or a mass fraction of about 0.001-0.01, about 0.002-0.007, or most about 0.01, at most about 0.005), acetaldehyde (in about 1-200 kg/hr, about 1-150 kg/hr, about 1-100 kg/hr, about 1-50 kg/hr, about 1-20 kg/hr, about 5-15 kg/hr, or at most about 200 kg/hr, at most about 150 kg/hr, at most about 100 kg/hr, at most about 50 kg/hr, at most about 20 kg/hr, at most about 15 kg/hr, or at most about 11 kg/hr or a mass fraction of at most about 0.001), succinic anhydride (in about 1-100 kg/hr, about 1-50 kg/hr, 1-10 kg/hr, about 1-5 kg/hr, or at most about 50 kg/hr, at most about 10 kg/hr, 5 kg/hr, or at most about 3 kg/hr), bPL (in about at most 2000 kg/hr, at most about 1500 kg/hr, at most about 1000 kg/hr, at most about 500 kg/hr, 200 kg/hr, at most about 300 kg/hr, at most about 500 kg/hr, at most about 550 kg/hr, or at most about 600 kg/hr, or a mass fraction of at most 0.1, at most about 0.075, at most about 0.05, or at most about 0.043), and carbonylation catalyst or components thereof from the solvent feed. In some embodiments, the mass fraction of solvent from the solvent feed can be at least about 0.85, at least about 0.9, at least about 0.94, or at least about 0.95. In some embodiments, the mole fraction of solvent from the solvent feed can be at least about 0.85, at least about 0.9, at least about 0.94, or at least about 0.95.

[0231] In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a solvent feed at least about 1000 kg/hr, at least about 750 kg/hr, at least about 600 kg/hr, at least about 530 kg/hr, at least about 500 kg/hr, at least about 250 kg/hr, at least about 100 kg/hr, at least about 75 kg/hr, at least about 60 kg/hr, at least about 53 kg/hr, or at least about 50 kg/hr. In some embodiments, the inlet to the carbonylation reaction system can receive carbonylation catalyst from a solvent feed at least about 1 kmol/hr, at least about 0.8 kmol/hr, at least about 0.75 kmol/hr, at least about 0.56 kmol/hr, or at least about 0.5 kmol/hr, at least about 0.25 kmol/hr, at least about 0.1 kmol/hr, at least about 0.1 kmol/hr, at least about 0.075 kmol/hr, at least about 0.056 kmol/hr, or at least about 0.05 kmol/hr. In some

embodiments, the mass fraction of carbonylation catalyst from the solvent feed can be at least about 0.0002, at least about 0.002, at least about 0.003, or at least about 0.004.

[0232] In some embodiments, the inlet to the carbonylation reaction system can receive a solvent feed at a temperature between about 10-100°C, between about 20-50°C, between about 25-45°C, between about 30-40°C, or about 36.6°C. In some embodiments, the inlet to the carbonylation reaction system can receive a solvent feed at a pressure of at least about 50 bar, about 60-70 bar, or at least about 65 bar.

Other Feed Sources

[0233] The β-propiolactone production system/production process may further include other feed sources. For example, in one variation, the β-propiolactone production system/production process further includes a Lewis base additive source.

[0234] In some embodiments, a Lewis base additive may be added to the carbonylation reactor. In certain embodiments, such Lewis base additives can stabilize or reduce deactivation of the catalysts. In some embodiments, the Lewis base additive is selected from the group consisting of phosphines, amines, guanidines, amidines, and nitrogen-containing heterocycles. In some embodiments, the Lewis base additive is a hindered amine base. In some embodiments, the Lewis base additive is a 2,6-lutidine; imidazole, 1-methylimidazole, 4-dimethylaminopyridine, trihexylamine and triphenylphosphine.

[0235] The exemplary system depicted in FIG. **14** also includes carbonylation product stream 1414, post-isolation carbonylation product stream 1416, BPL purified stream 1418, PPL product stream 1420, and GAA product stream 1422.

Reactor

[0236] In some embodiments, the carbonylation reaction system can include at least one reactor for the carbonylation reaction. In some embodiments, the carbonylation system can include multiple reactors in series and/or parallel for the carbonylation reaction. In some

embodiments, the reactor(s) can be a continuous reactor(s). Examples of suitable continuous reactors include but are not limited to tubular reactors (i.e., plug flow-type reactors), fixed bed reactors, fluid bed reactors, continuous stirred tank reactors ("CSTR"), heat exchanger reactors (e.g., shell and tube type reactor), loop reactors (e.g., Buss, jet, etc.), membrane reactors, or other reactors known to those of ordinary skill in the art. In some embodiments, the carbonylation reaction system includes one or more CSTRs. All inlets and outlets to the carbonylation reaction system can include sensors that can determine the flowrate, composition (especially water and/or oxygen content), temperature, pressure, and other variables known to those of ordinary skill in the art. In addition, the sensors can be connected to control units that can control the various streams (i.e., feed controls) in order to adjust the process based on the needs of the process determined by the sensor units. Such control units can adjust the quality as well as the process controls of the system.

[0237] In some variations, the reactor in the β-propiolactone production system/production process is configured to receive the catalyst, ethylene oxide and carbon monoxide in certain ratios. In some embodiments, the ratio of catalyst to ethylene oxide is selected, based on other reaction conditions, so that the reaction proceeds in an economical and time-feasible manner. In some embodiments, the ratio of catalyst to ethylene oxide is about 1:10000 on a molar basis. In some embodiments, the molar ratio of catalyst to ethylene oxide is about 1:5000, is about 1:2500, is about 1:2000, is about 1:1500, is about 1:1000, is about 1:750, is about 1:500, is about 1:250, is about 1:200, is about 1:150, or is about 1:100. In some embodiments, the concentration of the ethylene oxide is in the range between about 0.1 M and about 5.0 M. In some embodiments, the concentration of the ethylene oxide is in the range between about 0.5 M and about 3.0 M.

[0238] In certain embodiments, the molar ratio of carbon monoxide to ethylene oxide in the reaction stream ranges from about 0.1:1 to about 100:1. In certain embodiments, the molar

ratio of carbon monoxide to ethylene oxide in the reaction stream is about 50:1, is about 20:1, is about 10:1, is about 5:1 or is about 1:1, or within a range including any two of these ratios. In some embodiments, the ratio of carbon monoxide to ethylene oxide is selected based on other reaction conditions so that the reaction proceeds in an economical and time-feasible manner.

[0239] In some variations, the reactor in the β-propiolactone production system/production process is configured to further receive one or more additional components. In certain embodiments, the additional components comprise diluents which do not directly participate in the chemical reactions of ethylene oxide. In certain embodiments, such diluents may include one or more inert gases (e.g., nitrogen, argon, helium and the like) or volatile organic molecules such as hydrocarbons, ethers, and the like. In certain embodiments, the reaction stream may comprise hydrogen, carbon monoxide of carbon dioxide, methane, and other compounds commonly found in industrial carbon monoxide streams. In certain embodiments, such additional components may have a direct or indirect chemical function in one or more of the processes involved in the conversion of ethylene oxide to β-propiolactone and various end products. Additional reactants can also include mixtures of carbon monoxide and another gas. For example, as noted above, in certain embodiments, carbon monoxide is provided in a mixture with hydrogen (e.g., Syngas).

[0240] Because the carbonylation reaction is exothermic, the reactors used can include an external circulation loop for reaction mass cooling. In some embodiments, the reactors can also include internal heat exchangers for cooling. For example, in the case of a shell and tube type reactor, the reactors can flow through the tube part of the reactor and a cooling medium can flow through the shell of the reactor or vice versa. Heat exchanger systems can vary depending on layout, reactor selection, as well as physical location of the reactor. The reactors can employ heat exchangers outside of the reactors in order to do the cooling/heating or the

reactors can have an integrated heat exchanger such as a tube and shell reactor. For example, a CSTR can utilize a layout for heat rejection by pumping a portion of the reaction fluid through an external heat exchanger or a plug flow-type reactor can be an integrated unit that combines the reactor and the heat exchanger into a single unit. Additional reactor/heat exchanger systems and heat management systems can be found in US Patent Nos. 3,128,163; 4,759,313; 8,246,915, which are hereby incorporated by reference in their entirety. In some embodiments, heat can be removed from a CSTR by using a coolant in a reactor jacket, one or more internal cooling coils, lower temperature feeds and/or recycle streams, an external heat exchange with pump around loop, and/or other methods known by those of ordinary skill in the art. In some embodiments, heat can be removed from a plug flow type reactor or a loop reaction by using a coolant in the reactor jacket and/or internal cooling coils. Furthermore, the reaction can occur on the tube side or the shell side of a shell and tube reactor and the other side can have the cooling medium. In addition, the reactors may have multiple cooling zones with varying heat transfer areas and/or heat transfer fluid temperatures and flows.

[0241] The type of reactor employed and the type of heat exchanger employed (either external or integrated) can be a function of various chemistry considerations (e.g., reaction conversions, by-products, etc.), degree of exotherm produced, and the mixing requirements for the reaction.

[0242] Since carbonylation reactions are exothermic reactions and the BPL purification system and thermolysis requires energy, it is possible to integrate at least some of the components between the carbonylation reaction system and the BPL purification system and/or thermolysis system. For example, steam or tempered water or other appropriate heat transfer media can be produced in a heat exchanger of the carbonylation reaction system and transported to the BPL purification system for heating a distillation column for example. In addition, the BPL purification system and the carbonylation reaction system may be integrated

into a single system or unit so that the heat produced from the carbonylation reaction can be used in the BPL purification system (in an evaporator or distillation column). The steam can be generated in a heat exchanger (e.g., shell and tube heat exchanger, reactor's cooling jacket, etc) via a temperature gradient between reaction fluids and water/steam of the heat exchanger. Steam can be used for heat integration between exothermic units (carbonylation reaction, polymerization reaction) and endothermic units (BPL purification system's columns/evaporators and thermolysis reaction). In some embodiments, steam is only used for heat management and integration and will not be introduced directly into the production processes.

[0243] As previously described, water and oxygen can damage the carbonylation catalyst. As such, oxygen and water intrusion into the carbonylation system should also be minimized. As such, the reactor seals may utilize a magnetic drive, a double mechanical seal, and/or materials of construction that are compatible with the reactants and products of the carbonylation reaction but not permeable to atmosphere. In some embodiments, the materials of construction of the reactor include metals. In some embodiments, the metals can be stainless steel. In some embodiments, the metals can be carbon steel. In some embodiments, the metals can be metal alloys such as nickel alloys. In some embodiments, the metals are chosen when compatibility or process conditions dictate, e.g., high chloride content or if carbon steel catalyzes EO decomposition. In some embodiments, everything up until the polymerization reaction system can include carbon steel. One of the benefits of carbon steel over stainless steel is its cost. In some embodiments, the metals can have a surface finish so as to minimize polymer nucleation sites. The materials of construction of the reactor can also include elastomer seals. In some embodiments, the elastomer seals are compatible with the reactants and products of the carbonylation reaction but not permeable to the atmosphere. Examples of elastomer seals include but are not limited to Kalrez 6375, Chemraz 505, PTFE-encapsulated

Viton, and PEEK. The materials of construction of external parts of the carbonylation reaction system can be compatible with the environment, for example, compatible with sand, salty water, not heat absorbing, and can protect the equipment from the environment.

[0244] In some embodiments, the carbonylation reaction system is operated so as to minimize or mitigate PPL and polyethylene oxide formation prior to the polymerization reaction system. In some embodiments, the carbonylation reaction system is operated so as to avoid catalyst decomposition.

[0245] In some embodiments, the carbonylation reactor(s) can have a downstream flash tank with a reflux condenser to separate unreacted carbon monoxide as a recycled carbon monoxide stream from the carbonylation reaction system. As previously described, the recycled carbon monoxide stream can be sent to a CO compressor and/or combined with a fresh carbon monoxide feed prior to being sent back into the carbonylation reaction system. The flash tank can separate most of the CO to avoid its separation downstream, especially in the carbonylation catalyst isolation system. In some embodiments, excess gas is removed or purged from the reactor itself and thus a flash tank is not necessary.

[0246] In some embodiments, the carbonylation reactor(s) can operate at a temperature of about 40-100°C, about 50-90°C, about 60-80°C, about 65-75°C, or about 70°C. In some embodiments, the reaction temperature can range from between about -20 °C, to about 600 °C. In some embodiments, the reaction temperature is about -20 °C, about 0 °C, about 20 °C, about 40 °C, about 60 °C, about 80 °C, about 100 °C, about 200 °C, about 300 °C, about 400 °C, about 500 °C or about , about 600 °C. In some embodiments, the temperature is in a range between about 40 °C and about 120 °C. In some embodiments, the temperature is in a range between about 60 °C and about 140 °C. In some embodiments, the temperature is in a range between about 40 °C and about 80 °C. In some embodiments, the temperature is in a range between about 50 °C and about 70 °C. In some embodiments, the reactants, catalyst and solvent

are supplied to the reactor at standard temperature, and then heated in the reactor. In some embodiments, the reactants are pre-heated before entering the reactor.

[0247] In some embodiments, the carbonylation reactor(s) can operate at a pressure of about 600-1200 psig, about 700-1100 psig, about 800-1000 psig, about 850-950 psig, or about 900 psig. In some embodiments, the reaction pressure can range from between about 50 psig to about 5000 psig. In some embodiments, the reaction pressure is about 100 psig, about 200 psig, about 300 psig, about 400 psig, about 500 psig, about 600 psig, about 700 psig, about 800 psig, about 900 psig, or about 1000 psig. In some embodiments, the pressure ranges from about 50 psig to about 2000 psig. In some embodiments, the pressure ranges from about 100 psig to 1000 psig. In some embodiments, the pressure ranges from about 200 psig to about 800 psig. In some embodiments, the pressure ranges from about 800 psig to about 1600 psig. In some embodiments, the pressure ranges from about 1500 psig to about 3500 psig. In some embodiments, the pressure ranges from about 3000 psig to about 5500 psig. In some embodiments, the reaction pressure is supplied entirely by the carbon monoxide. For example, carbon monoxide is added to the reactor at high pressure to increase pressure to the reaction pressure. In some embodiments, all reactants, solvent and catalyst are supplied to the reactor at reaction pressure.

[0248] In some embodiments, the reaction is maintained for a period of time sufficient to allow complete, near complete reaction of the ethylene oxide to carbonylation products or as complete as possible based on the reaction kinetics and or reaction conditions. In some embodiments, the reaction time is a residence time in the carbonylation reactor in step (a). In certain embodiments, the residence time is about 12 hours, about 8 hours, about 6 hours, about 3 hours, about 2 hours or about 1 hour. In certain embodiments, the residence time is about 30 minutes, about 20 minutes, about 15 minutes, about 10 minutes, about 5 minutes, about 3

minutes, about 2 minutes, or about 1 minute. In certain embodiments, the residence time is less than 1 minute.

[0249] The chemistry involved in a carbonylation reaction system can include, but are not limited to, the following three reactions: (1) CO + EO → bPL; (2) EO → acetaldehyde; (3) bPL → succinic anhydride. The conversions for the three reactions may vary depending on many factors including amount of reactants, amount of catalyst, temperature, pressure, flow rate, etc. However, the first reaction can have an EO conversion of about 0.2-0.999, about 0.5-0.95, about 0.6-0.9, about 0.7-0.8, or about 0.75. The second reaction can have an EO conversion of about 0-0.1, about 0.001-0.02, about 0.002-0.01, or about 0.005. The third reaction can have a bPL conversion of about 0.0002-0.02, about 0.0005-0.01, about 0.001-0.003, or about 0.002.

[0250] FIG. **15** illustrates an exemplary embodiment of a carbonylation reaction system disclosed herein. Carbonylation reaction system **1513** can include carbonylation reaction system inlet **1509** for carbonylation reactor **1525**. As previously described, the inlet can be made up of multiple inlets or feeds into the reaction system. In addition, carbonylation reaction system **1513** includes flash tank **1526** with condenser **1527**. Flash tank **1526** and condenser **1527** separate the reactor product stream into recycled carbon monoxide stream **1510** and carbonylation product stream **1514**.

Carbonylation Product Stream (i.e., BPL Product Stream)

[0251] In some embodiments, the carbonylation product stream includes at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 8000 kg/hr bPL, at least about 12000 kg/hr bPL, at least about 16000 kg/hr bPL, at least about 20000 kg/hr bPL, at least about 25000 kg/hr bPL, at least about 30000 kg/hr bPL, at least about 35000 kg/hr bPL, at least about 36380 kg/hr bPL, or at least about 40000 kg/hr bPL. In some

embodiments, the carbonylation product stream includes between about 2000 kg/hr bPL and about 4000 kg/hr bPL, about 2500 kg/hr bPL and about 4000 kg/hr bPL, about 3000 kg/hr bPL and about 4000 kg/hr bPL, about 3500 kg/hr bPL and about 4000 kg/hr bPL, about 3638 kg/hr bPL and about 4000 kg/hr bPL, between about 2000 kg/hr bPL and about 40000 kg/hr bPL, about 2500 kg/hr bPL and about 40000 kg/hr bPL, about 3000 kg/hr bPL and about 40000 kg/hr bPL, about 3500 kg/hr bPL and about 40000 kg/hr bPL, about 3638 kg/hr bPL and about 40000 kg/hr bPL, about 4000 kg/hr bPL and about 40000 kg/hr bPL, about 8000 kg/hr bPL and about 40000 kg/hr bPL, about 12000 kg/hr bPL and about 40000 kg/hr bPL, about 16000 kg/hr bPL and about 40000 kg/hr bPL, about 20000 kg/hr bPL and about 40000 kg/hr bPL, about 25000 kg/hr bPL and about 40000 kg/hr bPL, about 30000 kg/hr bPL and about 40000 kg/hr bPL, or about 35000 kg/hr bPL and about 40000 kg/hr bPL.

[0252] In some embodiments, the carbonylation product stream includes at least about 30 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 45 kmol/hr bPL, at least about 50 kmol/hr bPL, at least about 55 kmol/hr bPL, at least about 100 kmol/hr bPL, at least about 200 kmol/hr bPL, at least about 300 kmol/hr bPL, at least about 400 kmol/hr bPL, at least about 450 kmol/hr bPL, at least about 500 kmol/hr bPL, or at least about 550 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the carbonylation product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.2-0.23, at least about 0.15, at least about 0.2, or at least about 0.224. In some embodiments, the mole fraction of bPL in the carbonylation product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.21-0.23, at least about 0.15, at least about 0.2, or at least about 0.22. The carbonylation product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005-0.05, about 0.02-0.045, about 0.04, at most about 0.014, at most about 0.02, or at most about 0.05), unreacted carbon monoxide (in mass fraction of about 0.0005-0.01, at most about 0.01, or at most about 0.02), acetaldehyde (in mass fraction of about 0.0005-0.001, at most about

0.001, or at most about 0.002), succinic anhydride (in mass fraction of about 0.0005-0.001, at most about 0.001, or at most about 0.002), carbonylation catalyst (in about 40-640 kg/hr, about 45-600 kg/hr, about 50-600 kg/hr, about 50-300 kg/hr, about 50-100 kg/hr, about 40-64 kg/hr, about 45-60 kg/hr, about 50-60 kg/hr, at most 54.8 kg/hr, at most about 60 kg/hr, at most 300 kg/hr, or at most 600 kg/hr or a mass fraction of about 0.001-0.005, about 0.002-0.004, at most about 0.003, or at most about 0.004), and the remainder solvent. In some embodiments, the carbonylation product stream can include sufficient ethylene oxide so as to prevent anhydride formation.

[0253] In some embodiments, the carbonylation product stream from the carbonylation reaction system can have a temperature of about 50-100°C, about 60-90°C, about 65-75°C, or about 70°C. In some embodiments, the carbonylation product stream can have a pressure of about 1-5 bar, about 2-4 bar, or about 3 bar.

[0254] In some embodiments, the carbonylation reaction system has a selectivity of at least about 95%, at least about 97%, at least about 99%, at least about 99.5%, or at least about 99.8%. In some embodiments, the carbonylation reaction system has a yield of at least about 90%, at least about 95%, at least about 98%, at least about 99%, or at least about 99.5%. In some embodiments, the selectivity of bPL is the ratio of bPL yield to ethylene oxide conversion, wherein the bPL yield is measured relative to ethylene oxide. In other embodiments, the selectivity of bPL is the ratio of bPL yield to carbon monoxide conversion, wherein the bPL yield is measured relative to carbon monoxide.

Carbonylation Catalyst Recycle System

[0255] With reference again to FIG. **1**, the carbonylation catalyst recycle system may be employed to recover at least a portion of the carbonylation catalyst, or components thereof, present in the β-propiolactone product stream. Such recovered carbonylation catalyst may be recycled and reused in the β-propiolactone production system/production process.

[0256] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0257] Any suitable methods and techniques known in the art may be used to recover at least a portion of the carbonylation catalyst present in the β-propiolactone product stream. Such methods and techniques may include, for example, nanofiltration (as depicted in FIG. **1**), distillation, liquid-liquid extraction, ionic liquids, and ion exchange, or adsorption. Combinations of methods and techniques described herein may also be employed.

Nanofiltration

[0258] In some embodiments, the carbonylation catalyst recycle system involves the use of nanofiltration. For example, a nanofiltration membrane may be used. In some variations, the nanofiltration membrane is an organic solvent-stable nanofiltration membrane. Although any nanofiltration membrane may be used in combination with any organic solvent or organic solvent system compatible with the carbonylation reaction, the nanofiltration membrane may be selected in combination with the organic solvent or solvents such that the process achieves predetermined levels of lactone formation and catalyst-lactone separation. In some variations, the nanofiltration membrane is a polymeric nanofiltration membrane, while in other variations, the nanofiltration membrane is a ceramic nanofiltration membrane.

[0259] In some embodiments, the nanofiltration membrane is a polymeric membrane. Any suitable polymeric membranes may be used in the methods described herein. For example, in some variations, the polymeric membrane comprises polyimides, polyamide-imides, silicone-

coated polyamide composites, polyacrylonitriles, polydimethylsiloxane films on polyacrylonitrile supports, silcones, polyphosphazenes, polyphenylene sulfide, polyetheretherketone, or polybenzimidazol. In certain variations, the polymeric membrane has a silicone backbone.

[0260] In certain variations, the polymeric membrane is selected from polyimides, including those marketed under the trademark STARMEM by Membrane Extraction Technology Ltd (Wembley, UK) and integrally skinned asymmetric membranes made from polyimides, polyamide-imides, silicone-coated polyamide composites, polyacrylonitriles, polydimethylsiloxane films on polyacrylonitrile supports, silcones, polyphosphazenes, polyphenylene sulfide, polyetheretherketone, and polybenzimidazol. In some embodiments, the organic solvent is tetrahydrofuran and the nanofiltration membrane is an integrally skinned asymmetric polyimide membrane made from Lenzing P84 or a ST ARMEM® polyimide membrane. In some embodiments, the organic solvent is diethyl ether and the nanomembrane is a silicone-coated polyamide composite. In some embodiments, the nanofiltration membrane is a commercially available membrane. In other embodiments, the nanofiltration membrane is an integrally skinned asymmetric polyimide membrane made from Lenzing P84 and manufactured by GMT Membrantechnik GmbH (Rheinfelden, Germany). In some other embodiments, the nanofiltration membrane is a STARMEM® polyimide membrane from Membrane Extraction Technology Ltd (Wembley, UK) and the nanofiltration step is performed at a temperature under 50 °C and a pressure under 60 bar. In still other embodiments, the nanofiltration membrane is a silicone-coated organic solvent resistant polyamide composite nanofiltration membrane as disclosed in U.S. Patent No. 6,887,380, incorporated herein by reference.

[0261] In other variations, the nanofiltration membrane is a ceramic membrane comprising inorganic materials.

[0262] Nanofiltration membranes of various configurations may be employed in the carbonylation catalyst recycling system. For example, in some embodiments, the membrane is a plate-and-frame membrane. With reference to FIG. **3**, exemplary carbonylation catalyst recycle system **300** that uses membrane **310** is depicted. Feed **302** may include, for example, β-propiolactone, carbonylation solvent, small amounts of ethylene oxide and carbon monoxide, carbonylation catalyst, and by-products (such as acetaldehyde and succinic anhydride). Feed **302** is transferred to membrane via pumps **306** and **308**. Sensor **304** is positioned before pump **306** to regulate the rate at which feed **302** is pumped through membrane **310**. In some variations, sensor **304** may be a ultra-violet (UV) sensor. Other suitable sensors may also be employed. Feed **302** passes through membrane **310** by way of the transmembrane pressure, varied according to the pump set points. In some variations, membrane **310** is a plate-and-frame membrane, as depicted in FIG. **3**. However, in other variations, other suitable membranes may be used. For example, in other variation, membrane **310** of carbonylation catalyst recycle system **300** may be a spiral wound membrane or a tubular membrane, and such alternative configurations are discussed in further detail below.

[0263] With reference again to FIG. **3**, membrane **310** produces permeate stream **316** and retentate stream **324**. Permeate stream **316** may include, for example, β-propiolactone, carbonylation solvent, small amounts of ethylene oxide and carbon monoxide, by-products (such as acetaldehyde and succinic anhydride), and trace amounts of carbonylation catalyst. Further, permeate stream **316** may have a permeability of at least 0.5 L/m^2 hr bar, at least 0.6 L/m^2 hr bar, at least 0.7 L/m^2 hr bar, at least 0.8 L/m^2 hr bar, at least 0.9 L/m^2 hr bar, at least 1.0 L/m^2 hr bar, at least 1.1 L/m^2 hr bar, at least 1.2 L/m^2 hr bar, at least 1.3 L/m^2 hr bar, at least 1.4 L/m^2 hr bar, at least 1.5 L/m^2 hr bar, at least 1.6 L/m^2 hr bar, at least 1.7 L/m^2 hr bar, at least 1.8 L/m^2 hr bar, at least 1.9 L/m^2 hr bar, at least 2 L/m^2 hr bar, at least 2.5 L/m^2 hr bar, at least 3 L/m^2 hr bar, at least 3.5 L/m^2 hr bar, or at least 4 L/m^2 hr bar; or between 0.5 L/m^2 hr bar and 5

L/m^2 hr bar, or between 3 L/m^2 hr bar and 4.5 L/m^2 hr bar; or between 0.5 L/m^2 hr bar and 10 L/m^2 hr bar, or between 3 L/m^2 hr bar and 10 L/m^2 hr bar. In some variations, permeability (or membrane permeability) refers to volumetric flow rate of material that permeates through a specified surface area at a specified transmembrane pressure (TMP). In some variations, the transmembrane pressure is the pressure difference between the retentate side of the membrane and the permeate side of the membrane. In some embodiments, the relationship can be expressed as Permeability = Volumetric flow rate / (Surface Area x TMP). In some embodiments, permeability may be determined by measuring the flow rate of material which permeates across a membrane sample of known surface area at a known TMP.

[0264] Sensor **312** is positioned after membrane **310** to analyze the contents of permeate stream **316**. In some variations, sensor **312** may be a UV sensor. Other suitable sensors may also be employed.

[0265] Carbonylation catalyst recycle system **300** is configured to achieve a catalyst rejection of at least 80%, at least 85%, at least 90%, at least 91%, at least 92%, at least 93%, at least 94%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%, at least 99.1%, at least 99.2%, at least 99.3%, at least 99.4%, at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%, or 100%. In some variations, catalyst rejection refers to the percentage (by mass) of catalyst which permeates through the membrane compared to that which does not and is retained on the retentate side of the membrane. Catalyst rejection may be determined by any suitable method in the art, including, for example, using analytical instruments to detect catalyst concentrations at the membrane feed, permeate and retentate.

[0266] With reference again to FIG. **3**, pressure control valve **314** is positioned after sensor **312** and biased to upstream flash units. In some embodiments, pressure control valve (PCV) 314 can be used to control transmembrane pressure (TMP) which may affect performance of the membrane. Sensor 312 may detect catalyst rejection and provide a feedback signal to PCV

314 to make adjustments for system performance. PCV 314 may in some embodiments detect the pressure of the upstream flash tank and prevent volatile species (for example, carbon monoxide) from vaporizing as pressure changes across the membrane. Vaporization or flashing across the membrane may affect the durability of the membrane.

[0267] Retentate stream **324** may include, for example, carbonylation solvent, β-propiolactone, and carbonylation catalyst. Pump **322** may be used to transfer retentate stream **324** to the β-propiolactone production system/production process described herein (*e.g.*, to a carbonylation reactor of the β-propiolactone production system/production process). In some embodiments, catalyst may deactivate as it is circulated through the membrane system on the retentate side (for example, with exposure to oxygen or water). In certain embodiments, a portion of the retentate stream is purged for a period of time to avoid accumulation of deactivated catalyst within the system. Valve **320** is configured to purge the system and bleed **326**.

[0268] As discussed above, while FIG. **3** depicts the use of a plate-and-frame membrane, other membrane configurations may be employed. For example, in other embodiments, the membrane is a spiral wound membrane. In yet other embodiments, the membrane is a tubular membrane. In still other embodiments, the membrane is a pleated sheet membrane.

[0269] In one variation, the membrane is a polymeric membrane in a plate and frame configuration. In another variation, the membrane is a polymeric membrane in a spiral wound configuration. In yet another variation, the membrane is a ceramic membrane in a tubular configuration.

[0270] While FIG. **3** depicts the use of one membrane, in other variations, a plurality of membranes may be used. For example, at least two membranes connected in series may be used. In one variation, a plurality of plate-and-frame membranes connected in series may be used. In other variations, a plurality of spiral wound membranes connected in series may be

used. In other variations, a plate-and-frame membrane may be connected in series with a spiral wound membrane. It should be understood that the membrane configurations may be in series, in parallel, or in a combination of series and parallel. For example, in some embodiments, the membranes are configured in a "Christmas tree" configuration.

[0271] In one embodiment, the nanofiltration membrane is a polymeric, spiral wound membrane with a silicone backbone, carbonylation catalyst rejection rate of at least 99%, and permeability of at least 1 L/m^2 hr bar.

Distillation

[0272] In other embodiments, the carbonylation catalyst recycle system involves a distillation apparatus.

[0273] In some variations, the distillation apparatus recover at least a portion of the carbonylation catalyst present in the β-propiolactone product stream using a multi-solvent system. For example, in one variation, a two-solvent system may be used, wherein the first solvent has a boiling point above 166°C and may serve as the carrier of the catalyst, and the second solvent is selected to facilitate the carbonylation reaction.

[0274] In other variations, the distillation may include heating the β-propiolactone product stream to volatilize at least a portion of the β-propiolactone and/or the solvent to form a distillate, removing the distillate, and condensing the distillate. In other embodiments, the distillation is a vacuum distillation, wherein the distillate is formed by reducing the pressure of the β-propiolactone product stream. In certain embodiments, vacuum distillation allows at least a portion of the carbonylation catalyst to be removed from the β-propiolactone product stream without degradation of the catalyst at higher temperatures. In other variations, the distillation is performed by both increasing the temperature and decreasing the pressure of the β-propiolactone product stream. The carbonylation catalyst remaining the in the retained mixture after distillation can then be isolated for reuse in the carbonylation reaction using any methods

known in the art, including, for example, solvent-solvent extraction, nanofiltration, ionic liquids, or adsorption.

Liquid-Liquid Extraction

[0275] In other embodiments, the carbonylation catalyst recycle system involves a liquid-liquid extraction apparatus.

[0276] In some variations, the liquid-liquid extraction apparatus employs an extraction solvent in which the catalyst (or a component of the catalyst) is soluble or at least partially soluble. In other variations, the extraction solvent is one in which the β-propiolactone is soluble or at least partially soluble, but which has little tendency to dissolve the carbonylation catalyst (or one or more components of the carbonylation catalyst). In either case, the use of the extraction solvent results in the formation of two phases. In certain embodiments, the extraction solvent is a highly polar solvent such as water or an ionic liquid. In certain embodiments, the extraction solvent is supercritical CO_2. In certain embodiments, the extraction solvent is water or an aqueous solution. In certain embodiments, the extraction solvent is an ionic liquid. In certain embodiments where the solvent is an ionic liquid, the ionic liquid has a formula $[Cat^+][X^-]$ wherein $[Cat^+]$ refers to one or more organic cationic species; and $[X^-]$ refers to one or more anions. In certain embodiments, $[Cat^+]$ is selected from the group consisting of: ammonium, tetralkylammonium, benzimidazolium, benzofuranium, benzothiophenium, benzotriazolium, borolium, cinnolinium, diazabicyclodecenium, diazabicyclononenium, 1 ,4-diazabicyclo[2.2.2]octanium, diazabicyclo-undecenium, dithiazolium, furanium, guanidinium, imidazolium, indazolium, indolinium, indolium, morpholinium, oxaborolium, oxaphospholium, oxazinium, oxazolium, iso-oxazolium, oxothiazolium, phospholium, phosphonium, phthalazinium, piperazinium, piperidinium, pyranium, pyrazinium, pyrazolium, pyridazinium, pyridinium, pyrimidinium, pyrrolidinium, pyrrolium, quinazolinium, quinolinium, iso-quinolinium, quinoxalinium, quinuclidinium,

selenazolium, sulfonium, tetrazolium, thiadiazolium, iso-thiadiazolium, thiazinium, thiazolium, iso-thiazolium, thiophenium, thiuronium, triazinium, triazolium, iso-triazolium, uronium, and any combination of two or more of these. In accordance with the present invention, [X^-] may comprise an anion selected from halides, sulphates, sulfonates, sulfonimides, phosphates, phosphonates, carboxylates, CN^-, NO_3^-, NO_2^-, BF_4^- and PF_6^-.

[0277] In some embodiments, the extraction solvent includes pentane, cyclohexane, hexane, heptane, tetrahydrofuran, p-dioxane, 4-methyl-1,3-dioxolan-2-one, N,N-dimethylformamide, 1-methyl-2-pyrrolidinone, or sulfolane, or any combinations thereof. In one embodiment, the extraction solvent includes sulfolane and hexane. In another embodiment, the liquid-liquid extraction solvent includes sulfolane, hexane, and dioxane.

Precipitation

[0278] In certain embodiments, the carbonylation catalyst recycle system is configured to precipitate the carbonylation catalyst. Precipitation of the carbonylation catalyst may be accomplished by any known methods and techniques. Suitable means of precipitating the catalyst will be apparent to the skilled chemist and may include, but are not limited to: adding a solvent to the β-propiolactone product stream in which the catalyst (or a component thereof) is poorly soluble, cooling the β-propiolactone product stream, adding a material that interacts with the catalyst (or a component thereof) to form an insoluble adduct, removing solvent, excess feedstock, or carbon monoxide from the β-propiolactone product stream, and combinations of any two or more of these. In certain embodiments where the step of treating the β-propiolactone product stream to separate a portion of the carbonylation catalyst entails precipitation, the precipitation step comprises adding a solvent in which the catalyst (or a component of the catalyst) is poorly soluble. In certain embodiments, a non-polar solvent such as an aliphatic hydrocarbon, an aromatic hydrocarbon, or condensed phase CO_2 is added to precipitate the catalyst. In certain embodiments, a solvent selected from butane, pentane,

hexane, heptane, octane, cyclopentane, cyclohexane, decalin, higher alkanes, and mixtures of two or more alkanes is added to the β-propiolactone product stream to precipitate the catalyst or a catalyst component. In certain embodiments, a solvent selected from benzene, toluene, xylene, mesitylene, chlorobenzene, or other substituted benzene compounds is added to the β-propiolactone product stream to precipitate the catalyst or a catalyst component. In certain embodiments, supercritical CO_2 is added to the β-propiolactone product stream to precipitate the catalyst or a catalyst component. In certain embodiments where the carbonylation catalyst comprises the combination of a Lewis acidic metal complex and a metal carbonyl compound and a non-polar solvent is added to the β-propiolactone product stream, this causes precipitation of the Lewis acidic metal complex but leaves at least a portion of the metal carbonyl component of the catalyst behind in the β-propiolactone product stream. In embodiments where the catalyst is precipitated, the step of separating the carbonylation catalyst typically includes further steps to remove the precipitate from the product stream, such isolation steps are well known in the art and can include, but are not limited to filtration, sedimentation, centrifugation, coagulation, and combinations of two or more of these.

Adsorption

[0279] In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by adsorbing the carbonylation catalyst or components thereof. In some variations, adsorption can entail treating the product streams containing carbonylation catalyst with a solid adsorbing material. Suitable solid adsorbing materials may include inorganic substances, activated carbon, polymers, resins, or any combination of two or more of these. Suitable inorganic adsorbing materials may include silica gel, silicate minerals, clays, diatomaceous earth, Fuller's earth, ceramics, zirconias, molecular sieves and the like. Suitable polymers may include polystyrenes, polyacrylonitrile, polyimides, polyolefins, polyesters, polyethers, polycarbonates, polyisocyanates, and the like. Such polymers may

optionally include additional chemical functional groups to enhance their ability to adsorb carbonylation catalysts or catalyst components. Such functional groups may include acids (*e.g.*, sulfonic or carboxylic acids), coordinating groups (*e.g.*, amine, thiol, phosphine, nitrile, or boron groups), and/or bases, (*e.g.*, amine groups or nitrogen heterocycles). In certain cases, the adsorbing materials (*e.g.*, whether inorganic or polymeric) are acidic, basic, or have undergone chemical treatments to enhance the affinity of the catalyst. In embodiments where carbonylation catalyst is removed from the product streams containing carbonylation catalyst by adsorption, the adsorbent can be contacted with the product stream by any conventional method. This includes, but is not limited to: flowing the product streams containing carbonylation catalyst through a fixed bed of adsorbent; flowing the product streams containing carbonylation catalyst through a fluidized bed of adsorbent; flowing the product streams containing carbonylation catalyst through fabrics, meshes, or filtration plates comprising the adsorbent material; or slurrying the product streams containing carbonylation catalyst with the adsorbent material (typically followed by filtration, centrifugation, sedimentation or the like to remove the adsorbent from the product stream).

[0280] In embodiments where the β-propiolactone product stream is flowed through a column of adsorbent, it may be desirable to provide a plurality of such columns in parallel with a provision to switch the flow from one column to another. Thus when one column of adsorbent becomes saturated with catalyst, it can be switched out of the flow path and the flow diverted to a fresh column—in certain embodiments, the interval of time from when a column is placed in the flow path to when it is switched out of the flow path corresponds to the "first time interval" recited in the methods described herein. Where an adsorbent is used to remove catalyst from the β-propiolactone product stream, the inventive methods will typically include a step of desorbing the catalyst or catalyst component(s) from the adsorbent. Such desorption methods are well known in the art and will vary depending on the identity of the adsorbant and

the catalyst. Desorption can include treating with a polar solvent or solute which displaces the catalyst or catalyst component, or can comprise a reactive process where a reagent is added to the adsorbed catalyst to regenerate it or form a species which is less adhered to the adsorbing solid.

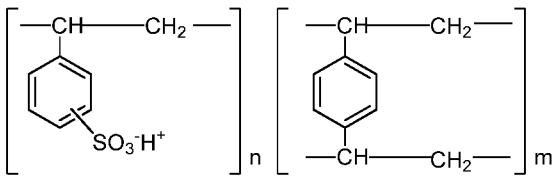
Ion Exchange

[0281] In certain embodiments, the carbonylation catalyst recycle system may be configured to separate the carbonylation catalyst by ion exchange of the carbonylation catalyst or components thereof. In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by treating the β-propiolactone product stream with ion exchange materials. The ion exchange materials may be, for example, cationic, anionic, amphoteric, Lewis basic, Lewis acidic, or may comprise chelating groups. In certain embodiments, the ion exchange material may be a cation exchanger. In certain embodiments, functional groups on the cation exchange materials may be selected from: $-SO_3$, PO_3^{2-}, –COOH, $-C_6H_4OH$, –SH, $-AsO_3$, or $-SeO_3$, or combinations of two or more of these. In certain embodiments, functional groups on the cation exchange materials comprise $-SO_3$

[0282] In certain embodiments, the ion exchange material may be an anion exchanger. In certain embodiments, functional groups on the anion exchange materials may be selected from: $-N^+(alkyl)_3$, $-N^+(CH_3)_3$, $-N^+(CH_3)_2C_2H_4OH$, $-N^+(CH_3)_2C_2H_5$, $-P^+(alkyl)_3$, $-P^+(aryl)_3$,$-P^+(C_4H_9)_3$, or $-P^+(Ph)_3$, or combinations of two or more of these. In certain embodiments, functional groups on the anion exchange materials comprise $-N^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(aryl)_3$.

[0283] In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by anion exchange and cation exchange. In certain embodiments, where the carbonylation catalyst comprises the combination of a cationic Lewis

acid and an anionic metal carbonyl, each is removed separately and the method comprises treating the β-propiolactone product stream with a cation exchange material to remove the Lewis acid and an anion exchange material to remove the metal carbonyl. In certain embodiments the anion and cation exchange are performed concomitantly. In certain embodiments, the anion and cation exchange are performed sequentially. In certain embodiments, the anion exchange is performed first followed by cation exchange. In certain embodiments, the cation exchange is performed first followed by anion exchange. In certain embodiments, an ion exchange material used in the separation step comprising an organic ion exchange resin may prove useful. Organic ion exchange resins generally possess a three dimensional structure, the matrix. Functional groups maybe attached to the structure, or directly incorporated in the polymeric chains. The matrix may be constructed from linear polymeric chains cross-linked with each other by relatively short links. By way of example, in various aspects, the present disclosure includes the use of ion exchange materials comprised of sulphonated polystyrene cross-linked with divinylbenzene:



[0284] In various aspects, ion exchange materials may take the form of gels, or gel resins, distributed across a bead, or other support substrate. In various aspects, ion exchange materials may take the form of macroporous resins which have a heterogeneous structure consisting of two phases, a gel region comprised of polymers and macroscopic permanent pores. In various embodiments of the present disclosure, the ion exchange materials comprise macroreticular resins which are additionally macroporous resins in which the gel regions consist of a plurality of bead micro-grains. Ion exchange materials may comprise a wide variety of morphologies and forms, including variations in porosity and other surface properties. In various aspects,

materials can be formed into, but not limited to beads, pellets, spheres, spheroids, rings, hollow cylinders, blocks, fibers, meshes, membranes, textiles.

[0285] In various aspects, the bead size may be widely distributed, or may be very narrow, so-called mono-disperse resins. In embodiments where catalyst is removed from the β-propiolactone product stream by ion exchange, the ion exchange material can be contacted with the product stream by any conventional method. This includes, but is not limited to: flowing the β-propiolactone product stream through a fixed bed of a solid ion exchange material (i.e. in the form of beads, granules or other particles); flowing the β-propiolactone product stream through a fluidized bed of adsorbent, flowing the β-propiolactone product stream through fabrics, meshes, or filtration plates comprising the ion exchange material, or slurrying the β-propiolactone product stream with the ion exchange material (typically followed by filtration, centrifugation, sedimentation or the like to remove the ion exchange material from the product stream). In embodiments where the β-propiolactone product stream is flowed through a packed column of ion exchange material, it may be desirable to provide a plurality of such columns in parallel with a provision to switch the flow from one to another periodically. Thus when one column of ion exchange material becomes saturated with catalyst, it can be switched out of the flow path and the flow diverted to a fresh column. In certain embodiments, the interval of time from when a column is placed in the flow path to when it is switched out of the flow path corresponds to the "first time interval" recited in the methods described herein.

[0286] Where an ion exchange material is used to remove catalyst from the β-propiolactone product stream, the inventive methods will typically include a subsequent step of removing the catalyst or catalyst component(s) from the ion exchange material. Such removal methods are well known in the art and typically involve contacting the ion exchange resin with a strong solution of a salt, the anion or cation of which will displace the catalyst component from the

ion exchange material. The specifics of this removal step may vary depending on the identity of the adsorbent and the catalyst, but suitable methods are known to those skilled in the art.

Ionic Liquids

[0287] In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst by using ionic liquids. For example, in some embodiments, In certain embodiments, the carbonylation catalyst recycle system is configured to separate the carbonylation catalyst using an ionic liquid to form a biphasic system comprising an ionic liquid phase and a β-propiolactone product stream. At least a portion of the catalyst (or a component thereof) is extracted into the ionic liquid phase, such that the concentration of catalyst is reduced in the reaction product phase. The ionic liquid phase comprising at least a portion of the carbonylation catalyst is then removed, the carbonylation catalyst is isolated from the ionic liquid phase using any suitable methods known in the art, and the isolated carbonylation catalyst is recycled back into the carbonylation reactor. For example, in some embodiments the carbonylation catalyst is isolated from the ionic liquid phase using, nanofiltration or precipitation. It may also be possible at times to use an ion exchange resin for such separation.

[0288] Any suitable ionic liquid known in the art may be used. In some embodiments, a mixture of ionic liquids is used.

Materials of Construction

[0289] The materials of construction suitable for the carbonylation catalyst recycling system may use any materials that are compatible with, for example, the membrane used. In some variations, the carbonylation catalyst recycling system has inert, metal surfaces, for example, to reduce or eliminate polymer nucleation sites.

[0290] In other variations, the carbonylation catalyst recycling system may use elastomer seals that are compatible with ethylene oxide, carbon monoxide and/or β-propiolactone, and

has little to no permeability to atmosphere. Examples may include: Kalrez 6375, Chemraz 505, PTFE encapsulated Viton, and PEEK.

[0291] In yet other variations, the materials of construction of external parts of the carbonylation catalyst recycling system may be compatible with the environment, including, for example, sand and salty water, and is not heat absorbing. Further, safety interlocks and safe operating parameters may be employed. For example, the carbonylation catalyst recycling system may be configured to mitigate polypropiolactone formation prior to the polypropiolactone production system/production process, and/or to avoid catalyst decomposition (*e.g.*, by addition of CO pressure on permeate or retentate side).

β-Propiolactone Product Stream Entering Carbonylation Catalyst Recycling System

[0292] With reference again to FIG. **1**, the β-propiolactone product stream from the β-propiolactone production system/production process is transferred to the carbonylation catalyst recycling system. In some embodiments, the β-propiolactone product stream includes at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 5000 kg/hr bPL, at least about 1000 kg/hr bPL, at least about 20000 kg/hr bPL, at least about 35000 kg/hr bPL, at least about 36380 kg/hr bPL, or at least about 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes about 2000 kg/hr bPL, about 2500 kg/hr bPL, about 3000 kg/hr bPL, about 3500 kg/hr bPL, about 3638 kg/hr bPL, about 4000 kg/hr bPL, about 5000 kg/hr bPL, about 1000 kg/hr bPL, about 20000 kg/hr bPL, about 35000 kg/hr bPL, about 36380 kg/hr bPL, or about 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes between about 2000 kg/hr bPL and 4000 kg/hr bPL, between about 2500 kg/hr bPL and 4000 kg/hr bPL, between about 3000 kg/hr bPL and 4000 kg/hr bPL, between about 3500 kg/hr bPL and 4000 kg/hr bPL, between about 3638 kg/hr bPL and 4000 kg/hr bPL, between about 2000 kg/hr bPL and 40000 kg/hr bPL, between about

2500 kg/hr bPL and 40000 kg/hr bPL, between about 3000 kg/hr bPL and 40000 kg/hr bPL, between about 3500 kg/hr bPL and 40000 kg/hr bPL, between about 3638 kg/hr bPL and 40000 kg/hr bPL, between about 4000 kg/hr bPL and 40000 kg/hr bPL, between about 5000 kg/hr bPL and 40000 kg/hr bPL, between about 1000 kg/hr bPL and 40000 kg/hr bPL, between about 20000 kg/hr bPL and 40000 kg/hr bPL, between about 35000 kg/hr bPL and 40000 kg/hr bPL, between about 36380 kg/hr bPL and 40000 kg/hr bPL, or between about 40000 kg/hr bPL and 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes at least about 30 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 45 kmol/hr bPL, at least about 50 kmol/hr bPL, at least about 55 kmol/hr bPL, at least about 100 kmol/hr bPL, at least about 200 kmol/hr bPL, at least about 300 kmol/hr bPL, at least about 400 kmol/hr bPL, at least about 450 kmol/hr bPL, at least about 500 kmol/hr bPL, or at least about 550 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.2-0.23, at least about 0.15, at least about 0.2, or at least about 0.224. In some embodiments, the mole fraction of bPL in the β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.21-0.23, at least about 0.15, at least about 0.2, or at least about 0.22. The β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005-0.05, about 0.01-0.045, about 0.04, at most about 0.014, at most about 0.02, or at most about 0.05), unreacted carbon monoxide (in mass fraction of about 0.0005-0.01, at most about 0.01, or at most about 0.02), acetaldehyde (in mass fraction of about 0.0005-0.005, at most about 0.005, or at most about 0.01), succinic anhydride (in mass fraction of about 0.0005-0.005, at most about 0.005, or at most about 0.001), carbonylation catalyst (in about 40-640 kg/hr, 300-640 kg/hr, 40-300 kg/hr, 40-64 kg/hr, about 45-60 kg/hr, about 50-60 kg/hr, at most 54.8 kg/hr, at most 60 kg/hr, at most 100 kg/hr, at most 300 kg/hr, or at most about 600 kg/hr or a mass fraction of about 0.001-0.005, about 0.002-0.004, at most about 0.003, or at most

about 0.004), and the remainder solvent. In some embodiments, the β-propiolactone product stream includes carbonylation catalyst components (in about 40-640 kg/hr, 300-640 kg/hr, 40-300 kg/hr, 40-64 kg/hr, about 45-60 kg/hr, about 50-60 kg/hr, at most 54.8 kg/hr, at most 60 kg/hr, at most 100 kg/hr, at most 300 kg/hr, or at most about 600 kg/hr or a mass fraction of about 0.001-0.005, about 0.002-0.004, at most about 0.003, or at most about 0.004).

[0293] In some embodiments, the β-propiolactone product stream from the β-propiolactone production system/production process can have a temperature of about 40-100°C, about 50-90°C, about 65-75°C, or about 70°C. In some embodiments, the β-propiolactone product stream can have a pressure of about 1-15 bar, about 2-10 bar, or about 7 bar.

β-Propiolactone Product Stream Exiting Carbonylation Catalyst Recycling System

[0294] In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system includes at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3100 kg/hr bPL, at least about 3200 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 5000 kg/hr bPL, at least about 1000 kg/hr bPL, at least about 20000 kg/hr bPL, or at least about 35000 kg/hr bPL. In some embodiments, the β-propiolactone product stream includes about 2000 kg/hr bPL, about 2500 kg/hr bPL, about 3000 kg/hr bPL, about 3500 kg/hr bPL, about 3638 kg/hr bPL, about 4000 kg/hr bPL, about 5000 kg/hr bPL, about 1000 kg/hr bPL, about 20000 kg/hr bPL, about 35000 kg/hr bPL, about 36380 kg/hr bPL, or about 40000 kg/hr bPL. In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system includes between about 2000 kg/hr bPL and 3500 kg/hr bPL, between about 2500 kg/hr bPL and 3500 kg/hr bPL, between about 3000 kg/hr bPL and 3500 kg/hr bPL, between about 2000 kg/hr bPL and 35000 kg/hr bPL, between about 2500 kg/hr bPL and 35000 kg/hr bPL, between about 3000 kg/hr bPL and 35000 kg/hr bPL, between about 3500 kg/hr bPL and 35000 kg/hr bPL, between about 3638 kg/hr bPL and 35000 kg/hr

bPL, between about 4000 kg/hr bPL and 35000 kg/hr bPL, between about 5000 kg/hr bPL and 35000 kg/hr bPL, between about 1000 kg/hr bPL and 35000 kg/hr bPL, or between about 20000 kg/hr bPL and 35000 kg/hr bPL. In some embodiments, the post-isolation β-propiolactone product stream includes at least about 30 kmol/hr bPL, at least about 35 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 43 kmol/hr bPL, at least about 45 kmol/hr bPL, at least about 100 kmol/hr bPL, at least about 200 kmol/hr bPL, at least about 300 kmol/hr bPL, or at least about 350 kmol/hr bPL In some embodiments, the mass fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.2-0.24, at least about 0.15, at least about 0.2, or at least about 0.225. In some embodiments, the mole fraction of bPL in the post-isolation β-propiolactone product stream can be about 0.1-0.4, about 0.15-0.3, about 0.18-0.25, about 0.21-0.23, at least about 0.15, at least about 0.2, or at least about 0.22. The post-isolation β-propiolactone product stream can also include other components including unreacted ethylene oxide (in mass fraction of about 0.005-0.05, about 0.01-0.04, about 0.044, at most about 0.014, at most about 0.02, or at most about 0.05), unreacted carbon monoxide (in mass fraction of about 0.0005-0.001, at most about 0.001, or at most about 0.002), acetaldehyde (in mass fraction of about 0.0005-0.005, at most about 0.005, or at most about 0.01), succinic anhydride (in mass fraction of about 0.0005-0.0051, at most about 0.005, or at most about 0.01), carbonylation catalyst (in about 0-50 kg/hr, about 0.5-20 kg/hr, about 1-15 kg/hr, about 0-5 kg/hr, about 0.5-2 kg/hr, about 1-1.5 kg/hr, at most 1.4 kg/hr, at most about 2 kg/hr, at most 10 kg/hr, or at most 20 kg/hr), and the remainder solvent. In some variations, the post-isolation β-propiolactone product stream can includes carbonylation catalyst components (in about 0-50 kg/hr, about 0.5-20 kg/hr, about 1-15 kg/hr, about 0-5 kg/hr, about 0.5-2 kg/hr, about 1-1.5 kg/hr, at most 1.4 kg/hr, at most about 2 kg/hr, at most 10 kg/hr, or at most 20 kg/hr).

[0295] In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system can have a temperature of about 20-60°C, about 30-50°C, about 35-45°C, or about 40°C. In some embodiments, the β-propiolactone product stream exiting the carbonylation catalyst recycling system can have a pressure of about 1-15 bar, about 2-10 bar, or about 7 bar.

Carbonylation Catalyst Regeneration and Accumulation

[0296] The carbonylation catalyst may be recovered from the catalyst recycling system in a form other than as active catalyst. Thus, with reference to FIG. **3**, in some variations, retentate stream **324** may require further processing by one or more additional steps to regenerate the carbonylation catalyst for use in the β-propiolactone production system/production process.

[0297] Further, the carbonylation catalyst (or a component thereof) separated from the β-propiolactone product stream may be accumulated through some interval of time. The accumulated catalyst (or component) forms a spent catalyst batch that is eventually reused (either in whole or in part) in a carbonylation process. The process for which the catalyst is re-used may or may not be the same process from which the catalyst was isolated. Likewise it may be reused for the same process but on another day or in a different reactor. This is in contrast to methods wherein the separated catalyst is treated as a stream within the reaction process which is returned to the reactor within a relatively short period.

[0298] In certain embodiments where the carbonylation catalyst comprises a cationic Lewis acid in combination with an anionic metal carbonyl, the cationic Lewis acid portion of the catalyst is captured from the β-propiolactone product stream without the associated metal carbonyl. In certain embodiments, the cationic Lewis acid is accumulated in a form with a counterion other than the anionic metal carbonyl. In such embodiments, the methods may include a further step of treating the accumulated batch of cationic Lewis acid under conditions

to swap a non-metal carbonyl anion associated with the accumulated Lewis acid with a metal carbonyl anion.

[0299] In certain embodiments where the carbonylation catalyst comprises a cationic Lewis acid in combination with an anionic metal carbonyl, the metal carbonyl portion of the catalyst is captured from the β-propiolactone product stream without the associated Lewis acid. The metal carbonyl thus accumulated may be captured as an anionic metal carbonyl (for example by anion exchange) or it may be accumulated in another form such as a reduced metal species, a metal salt, a neutral metal carbonyl, a mixed metal carbonyl complex, or some other form. In such embodiments, the methods may include a further step of treating the accumulated species to regenerate a catalytically active metal carbonyl compound. In the case where an intact metal carbonyl anion is accumulated (for example by capture on an anion exchange resin), such steps may include metathesis to free the metal carbonyl anion from the resin. This will typically entail flooding the resin with another anion (such as sodium chloride) to displace the metal carbonyl. The metal carbonyl may then be obtained as its sodium salt and utilized to produce active catalyst according to known catalyst synthesis procedures. Therefore, in certain embodiments, systems and methods described herein comprise further steps of freeing accumulated metal carbonyl anion from a resin. In certain embodiments, such steps entail further steps of utilizing accumulated metal carbonyl anion to regenerate active catalyst by combining the accumulated metal carbonyl with a suitable Lewis acid.

[0300] In certain embodiments, the metal carbonyl may be accumulated in a form other than as an intact metal carbonyl anion. For example, in CO-deficient atmospheres, the metal carbonyl may lose one or more CO ligands to form multinuclear metal carbonyl species, salts, or precipitate in elemental form. In other embodiments, a strong ligand may be utilized to displace one or more CO ligands and aid in capture of the metal carbonyl as a new complex. It is known that such species can be utilized to regenerate well defined metal carbonyl compounds

by treatment under CO pressure. Therefore, in certain embodiments, systems and methods described herein include further steps of regenerating the catalytically active metal carbonyl species from a non-catalytically active material accumulated from the β-propiolactone product stream. In certain embodiments, such steps entail further steps of treating accumulated residue derived from a catalytically active metal carbonyl compound under conditions to regenerate a catalytically active metal carbonyl suitable for reuse. In certain embodiments, such steps include a step of treating the accumulated residue under high CO pressure. In certain embodiments, methods include the step of treating a cobalt-containing residue accumulated from the β-propiolactone product stream under conditions of high CO pressure to convert it to dicobalt octacarbonyl.

[0301] In certain embodiments where the accumulation of catalyst separated from the β-propiolactone product stream comprises steps of recovering two or more separate catalyst components in separate recovered catalyst batches, additional steps of recombining recovered catalyst components may be needed to produce active carbonylation catalyst. In some cases the recovered catalyst components may be combined directly while in other steps one or more of the components may require processing as described above prior to step of combining. In certain embodiments such steps entail a metathesis to recombine a recovered cationic Lewis acid with a recovered metal carbonyl anion such as a carbonyl cobaltate.

[0302] The time interval required to accumulate a batch is dependent on the mode of accumulation, and the scale and economics of any processes required to transform the accumulated catalyst residue into active catalyst. In some embodiments, the time interval for accumulation of the catalyst or residue is on the order of hours to days, but may be weeks. Therefore, in certain embodiments of any of the methods described above, the first time interval is in the range from about 1 hour to about 200 hours. In certain embodiments, the first time interval is from about 2 hours to about 8 hours, from about 4 hours to about 16 hours, from

about 12 hours to about 24 hours, or from about 16 hours to about 36 hours. In certain embodiments, the first time interval is from about 1 day to about 20 days, from about 1 day to about 3 days, from about 2 days to about 5 days, from about 5 days to about 10 days, or from about 10 days to about 20 days.

[0303] During this time, the carbonylation reactor may be fed from a reservoir of catalyst which is depleted as the amount of accumulated catalyst (or catalyst residue) increases on the back end of the process. Additional time may be required to process the accumulated catalyst or catalyst residue to remanufacture active catalyst. Therefore, in some variations, some multiple of the first time interval have elapsed from the first time interval when the catalyst was accumulated to the later time at which the carbonylation reactor is fed with a catalyst feed stream containing catalyst derived from the catalyst accumulated during the first time interval. In certain embodiments the length of time between the second time interval (during with catalyst recovered is fed to reactor), and the first time interval (during which the catalyst was accumulated) is on the order of about 1 to about 100 times the length of the first time interval. In other words, if the first time interval is 10 hours, the second time interval would occur from about 10 hours to about 2000 hours after the completion of the accumulation step. In certain embodiments, the length of time between the second time interval and the first time interval is from about 1 to about 10 times the length of the first time interval. In certain embodiments, the length of time between the second time interval and the first time interval is from about 1 to about 3 times, from about 2 to about 5 times, from about 4 to about 10 times, from about 10 to about 50 times, from about 40 to about 80 times, or from about 50 to about 100 times, the length of the first time interval. In certain embodiments, the length of time between the second time interval and the first time interval is greater than 100 times the first time interval.

Continuous Replacement of Catalyst at Predetermined Rate

[0304] In certain variations, the carbonylation catalyst recycling system may be configured to continuously or intermittently introduce to the carbonylation reactor a catalyst replacement component that is different from the carbonylation catalyst (*e.g.*, from the carbonylation catalyst source) and may comprise a species selected from the group consisting of the Lewis acid, a precursor to the Lewis acid, the metal carbonyl, and a precursor to the metal carbonyl.

[0305] In some embodiments, the catalyst replacement component comprises the Lewis acid. In some embodiments, the catalyst replacement component comprises a precursor to the Lewis acid. In some embodiments, the catalyst replacement component comprises the metal carbonyl. In some embodiments, the catalyst replacement component comprises a precursor to the metal carbonyl.

[0306] In some embodiments, the catalyst replacement component is introduced at a rate that results in less than 10% variation in the rate of the carbonylation reaction over a period of one hour. In some embodiments, the catalyst replacement component is introduced at a rate that results in less than 5% variation in the rate of the carbonylation reaction over a period of one hour.

[0307] In some embodiments, the rate at which the catalyst replacement component is added to the carbonylation reactor is determined by the rate at which the carbonylation reaction rate has been observed to decrease. In some embodiments, the rate at which the one or more catalyst replacement components are added to the carbonylation reactor is directly proportional to the rate at which the carbonylation reaction rate has been observed to decrease.

[0308] In some embodiments, the one or more catalyst replacement components are introduced continuously to the carbonylation reactor at the same rate that the carbonylation reaction rate is observed to decrease. In some embodiments, the one or more catalyst replacement components are introduced intermittently to the carbonylation reactor to produce

an average rate which matches the rate at which the carbonylation reaction rate has been observed to decrease.

[0309] Thus, if the carbonylation reaction rate has been observed to decrease 5% over the course of a time period, the catalyst replacement component may either be added continuously or intermittently at such a rate that 5% of the initial amount of Lewis acid or metal carbonyl present in the carbonylation reactor is added over that same time period. In some embodiments, the catalyst replacement component is added continuously. In some embodiments, the catalyst replacement component is added every hour. In some embodiments, the catalyst replacement component is added every 30 minutes. In some embodiments, the catalyst replacement component is added every 15 minutes. In some embodiments, the catalyst replacement component is added every 10 minutes. In some embodiments, the catalyst replacement component is added every 5 minutes. In some embodiments, the catalyst replacement component is added every minute.

[0310] One of skill in the art will appreciate that the shorter the intervals at which the one or more catalyst replacement components are added, the less variation in the overall carbonylation reaction rate will be observed. It should be recognized, however, that this must be balanced against other considerations such as the complexity of making multiple additions.

Recycling to BPL Production system/production process

[0311] In some embodiments, the carbonylation catalyst and/or solvent stream may be recycled to the feed stream or to the carbonylation reactor. In some embodiments, the portion of the solvent and/or catalyst from the β-propiolactone product stream recycled to the carbonylation reactor or feed stream ranges from about 0% to about 100%. In some embodiments, the portion of the solvent and/or catalyst from the β-propiolactone product stream recycled to the carbonylation reactor or feed stream is about 100%, about 90%, about 80%, about 70%, about 60%, about 50%, about 40%, about 30%, about 20%, about 10%, or

about 0%. In some embodiments, a different percentage of the catalyst, as compared to the solvent is recycled, i.e., the proportions of either the catalyst or solvent component do not need to be equal.

BPL Purification System (and Solvent Recycle)

[0312] After the catalyst isolation system, the post-isolation carbonylation stream (i.e., post-isolation β-propiolactone product stream) can be fed to the BPL Purification system. The BPL purification system can separate bPL into a BPL purified stream from low-boiling impurities before it enters the polymerization reaction system, where high purity bPL can be required. In some embodiments, the BPL purified stream can have at least about 90 wt% bPL, at least about 95 wt% bPL, at least about 98 wt% bPL, at least about 99 wt% bPL, at least about 99.3 wt% bPL, at least about 99.5 wt% bPL, at least about 99.8 wt%, or at least about 99.9 wt%. In some embodiments, the BPL purified stream can have at most about 1 wt% solvent, at most about 0.5 wt% solvent, or at most about 0.1 wt% solvent. In some embodiments, the BPL purification system can also create a solvent recycle stream. In some embodiments, the BPL purification system can separate the bPL from the other components in the post-isolation carbonylation stream such as solvent, unreacted ethylene oxide, unreacted carbon monoxide, secondary reaction product acetaldehyde, secondary reaction product succinic anhydride, and carbonylation catalyst or components thereof that was not isolated in the catalyst isolation system. The separation of bPL from the other components in the post-isolation carbonylation stream can be accomplished by various methods known to those of ordinary skill in the art.

[0313] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen

compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0314] In some embodiments, the temperature in the BPL purification system can be at most about 150°C, at most about 125°C, at most about 115°C, at most about 105°C, or at most about 100°C. When bPL is exposed to temperatures greater than 100°C, the bPL can potentially decompose or be partially polymerized. Accordingly, the bPL can be purified without being exposed to temperatures of about 150 °C, 125 °C, 115 °C, 105 °C, or 100 °C.

[0315] In some embodiments, the separation is performed by exploiting the boiling point differential between the beta-propiolactone and the other components of the carbonylation product stream, primarily the solvent. In some embodiments, the boiling point of the solvent is lower than the boiling point of the beta-propiolactone. In some embodiments, the solvent is volatilized (e.g., evaporated) from the BPL purification feed along with other lighter components (e.g., ethylene oxide & acetaldehyde), leaving behind bPL, other heavier compounds (e.g., catalyst and succinic anhydride) and some leftover solvent from the BPL purification feed. In some embodiments, this includes exposing the BPL purification feed to reduced pressure. In some embodiments, this includes exposing BPL purification feed to increased temperature. In some embodiments, this includes exposing the BPL purification feed to both reduced pressure and increased temperature.

[0316] In some embodiments, the pressure is selected so that the boiling point of the solvent is reduced by about 5 °C as compared to the boiling point at atmospheric pressure. In some embodiments, the pressure is selected so the boiling point of the solvent is reduced by about 10 °C as compared to the boiling point at atmospheric pressure. In some embodiments, the pressure is selected so the boiling point of the solvent is reduced by about 20 °C as compared to the boiling point at atmospheric pressure. In some embodiments, the pressure is selected so

the boiling point of the solvent is reduced by about 50 °C as compared to the boiling point at atmospheric pressure.

[0317] In some embodiments, the increased temperature is above the boiling point of the solvent but below the boiling point of the beta-propiolactone, at the selected pressure. In some embodiments, the temperature is at least about 20 °C below the boiling point of the beta-propiolactone. In some embodiments, the temperature is at least about 30 °C below the boiling point of the beta-propiolactone. In some embodiments, the temperature is at least about 50 °C below the boiling point of the beta-propiolactone.

[0318] In some embodiments, the reduced pressure is in the range from about 1 Torr to about 760 Torr. In some embodiments, the pressure is in the range of about 1 Torr to about 400 Torr. In some embodiments, the pressure is in the range of about 5 Torr to about 200 Torr. In some embodiments, the pressure is in the range of about 10 Torr to about 100 Torr. In some embodiments, the pressure is in the range of about 20 Torr to about 50 Torr. In some embodiments, the pressure is about 50 Torr, about 100 Torr, about 150 Torr, about 200 Torr, about 250 Torr, about 300 Torr, about 400 Torr about 500 Torr, about 600 Torr or about 700 Torr.

[0319] In some embodiments, the separation step is performed at a pressure below about 100 Torr and at a temperature above about 120 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 100 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 50 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 110 °C. In some embodiments, the separation step is performed at a pressure below about 50 Torr and at a temperature above about 90 °C. In some embodiments, the separation step is performed at a pressure below about

20 Torr and at a temperature above about 60 °C. In some embodiments, the separation step is performed at a pressure below about 10 Torr and at a temperature above about 50 °C.

[0320] In some embodiments, the separation may be effected in a sequence of steps, each operating at an independent temperature and pressure. For example, in one embodiment, two steps may be used to obtain a more effective separation of beta-propiolactone, or a separate separation step may be used to isolate certain reaction by-products. In some embodiments, when a mixture of solvents is used, multiple separation steps may be required to remove particular solvents, individually or as a group, and effectively isolate the beta-propiolactone.

[0321] In certain embodiments, the separation of the beta-propiolactone from the BPL purification feed is performed in two stages. In some embodiments the process includes a preliminary separation step to remove one or more components of the BPL purification feed having boiling points below that of the beta-propiolactone product.

[0322] In some embodiments, the preliminary separation step includes separating the BPL purification feed into a gas stream comprising ethylene oxide, solvent, and bPL (and potentially carbon monoxide, acetaldehyde, and/or bPL); and a liquid stream comprising beta-propiolactone, carbonylation catalyst (and potentially succinic anhydride and/or solvent). In the second step of separation, the liquid stream is further separated into a beta-propiolactone stream comprising beta-propiolactone, a solvent stream comprising solvent, and potentially a catalyst and succinic anhydride purge stream. The gas stream can also be further separated into a solvent stream comprising solvent, a light gases stream comprising solvent and ethylene oxide (and potentially acetaldehyde), and a liquid bPL stream comprising bPL and solvent. The liquid bPL stream can join with the liquid stream prior to separation of the liquid stream and form a combined feed to the second separation step. In some embodiments, the solvent stream from the second separation step and/or the solvent stream from the gas stream separation

can form the solvent recycle stream which can be fed to the carbonylation reaction system or to a solvent reservoir.

[0323] In some embodiments where one or more solvents with a boiling point lower than that of the beta-propiolactone are present, the lower boiling solvent may be volatilized (e.g., evaporated) from the BPL purification feed in a preliminary separation step, leaving behind a mixture comprising catalyst, beta-propiolactone, other solvents (if any) and other compounds in the BPL purification stream which is then further treated to separate the beta-propiolactone stream.

[0324] In certain embodiments where the separation is performed in two stages, the first step of separation comprises exposing the reaction stream to mildly reduced pressure to produce the gas stream and the liquid stream. In certain embodiments where the separation is performed in two stages, the gas stream can be returned to the carbonylation step.

[0325] In certain embodiments, the separation of the beta-propiolactone from the BPL purification feed is performed in three stages. In the first step of separation, the BPL purification feed is separated into a gaseous stream comprising ethylene oxide, solvent, and bPL (and potentially carbon monoxide and/or acetalhydride); and a liquid stream comprising solvent, beta-propiolactone, and carbonylation catalyst (and potentially succinic anhydride). In the second step of separation, the gaseous stream is separated into a solvent side stream comprising solvent; a light gas stream comprising ethylene oxide and solvent (and potentially carbon monoxide and/or acetaldehyde); and second liquid stream comprising solvent and bPL. In the third step of separation, the second liquid stream and the first liquid stream are combined and separated into a gaseous solvent stream comprising solvent, a purified BPL stream comprising bPL, and potentially a catalyst and succinic anhydride purge stream. In some embodiments, the solvent side stream and/or the gaseous solvent stream can be used as the

solvent recycle stream for use in the carbonylation reaction system or can be stored in a solvent storage tank.

[0326] In certain embodiments where the separation is performed in three stages, the first step of separation comprises exposing the BPL purification feed to atmospheric pressure. In certain embodiments where the separation is performed in three stages, the second step of separation comprises exposing the gaseous stream to atmospheric pressure. In certain embodiments where the separation is performed in three stages, the third step of separation comprises exposing the gaseous stream to a vacuum or reduced pressure. In certain embodiments, the reduced pressure is between about 0.05-0.25 bara. In certain embodiments, the reduced pressure is between about 0.1-0.2 bara or about 0.15 bara.

[0327] In certain embodiments, the separation of the beta-propiolactone from the BPL purification feed is performed in four stages. In the first step of separation, the BPL purification feed is separated into a gaseous stream comprising ethylene oxide, solvent, and bPL (and potentially carbon monoxide and/or acetalhydride); and a liquid stream comprising solvent, beta-propiolactone, and carbonylation catalyst (and potentially succinic anhydride). In the second step of separation, the gaseous stream is separated into a solvent side stream comprising solvent; a light gas stream comprising ethylene oxide and solvent (and potentially carbon monoxide and/or acetaldehyde); and second liquid stream comprising solvent and bPL. In the third step of separation, the second liquid stream and the first liquid stream are combined and separated into a gaseous solvent stream comprising solvent, a purified BPL stream comprising bPL, and potentially a catalyst and succinic anhydride purge stream. In the fourth step of separation, the light gas stream is separated into a third solvent stream comprising solvent and a second light gas stream comprising ethylene oxide (and potentially carbon monoxide and/or acetaldehyde). In some embodiments, the solvent side stream, the gaseous solvent stream,

and/or the third solvent stream can be used as the solvent recycle stream for use in the carbonylation reaction system or can be stored in a solvent storage tank.

[0328] In certain embodiments where the separation is performed in four stages, the first step of separation comprises exposing the BPL purification feed to atmospheric pressure. In certain embodiments where the separation is performed in four stages, the second step of separation comprises exposing the gaseous stream to atmospheric pressure. In certain embodiments where the separation is performed in four stages, the third step of separation comprises exposing the combined liquid stream to a vacuum or reduced pressure. In certain embodiments, the reduced pressure is between about 0.05-0.25 bara. In certain embodiments, the reduced pressure is between about 0.1-0.2 bara or about 0.15 bara. In certain embodiments where the separation is performed in four stages, the fourth step of separation comprises exposing the light gas stream to atmospheric pressure.

[0329] In some embodiments, the BPL purification system can include at least one distillation column to separate bPL from the other components in the post-isolation carbonylation stream. In some embodiments, the BPL purification system includes at least two distillation columns. In some embodiments, the BPL purification system includes at least three distillation columns. In some embodiments, at least one of the distillation columns is a stripping column (i.e., stripper). In some embodiments, at least one of the distillation columns is a vacuum column. In some embodiments, the BPL purification system can include an initial evaporator, wherein the post-isolation carbonylation stream is first fed to an evaporator in the BPL purification system. The evaporator can perform a simple separation between the solvent and the bPL in the post-isolation carbonylation stream. The evaporator can reduce loads on subsequent distillation columns making them smaller. In some embodiments, the evaporator can reduce loads on subsequent distillation columns making them smaller by evaporating

solvent in the post-isolation carbonylation stream at about atmospheric pressure and about 100°C.

[0330] FIG. **16** illustrates an exemplary embodiment of the BPL Purification system disclosed herein.

Feed Stream

[0331] As depicted in FIG. **16**, in some embodiments of the exemplary system, feed **1616** to BPL purification system **1617** can be the post-isolation carbonylation product stream (i.e., post-isolation β-propiolactone product stream). In other embodiments, the feed to the BPL purification system can be the carbonylation product stream. In some embodiments, the feed to BPL purification system is at least about 10000 kg/hr, at least about 11000 kg/hr, at least about 12000 kg/hr, at least about 13000 kg/hr, at least about 13777 kg/hr, at least about 20000 kg/hr, at least about 50000 kg/hr, at least about 100000 kg/hr, at least about 110000 kg/hr, at least about 120000 kg/hr, at least about 130000 kg/hr, or at least about 137770 kg/hr. In some embodiments, the feed to BPL purification system is about 10000 kg/hr, about 11000 kg/hr, about 12000 kg/hr, about 13000 kg/hr, about 13777 kg/hr, about 20000 kg/hr, about 50000 kg/hr, about 100000 kg/hr, about 110000 kg/hr, about 120000 kg/hr, about 130000 kg/hr, or about 137770 kg/hr. In some embodiments, the feed to BPL purification system is between about 10000 kg/hr and about 13777 kg/hr, between about 11000 kg/hr and about 13777 kg/hr, between about 12000 kg/hr and about 13777 kg/hr, between about 13000 kg/hr and about 13777 kg/hr, between about 10000 kg/hr and 137770 kg/hr, between about 11000 kg/hr and about 137770 kg/hr, between about 12000 kg/hr and about 137770 kg/hr, between about 13000 kg/hr and about 137770 kg/hr, between about 13777 kg/hr and about 137770 kg/hr, between about 20000 kg/hr and about 137770 kg/hr, between about 50000 kg/hr and about 137770 kg/hr, between about 100000 kg/hr and about 137770 kg/hr, between about 110000 kg/hr and about 137770 kg/hr, between about 120000 kg/hr and about 137770 kg/hr, or between about

130000 kg/hr and about 137770 kg/hr. In some embodiments, the feed to BPL purification system has a bPL wt% between about 10-30, about 15-28, about 18-25, about 20-25, about 22-23, about 22.5, or at least 22.5. In some embodiments, the feed to BPL purification system has solvent (e.g., THF) wt% between 60-90, about 65-85, about 70-80, about 72-78, about 74-76, about 75, about 75.8, or at least about 75. In some embodiments, the feed to BPL purification system has a CO wt% between about 0-0.2, about 0.05-0.15, about 0.1, or at most about 0.2. In some embodiments, the feed to BPL purification system has an acetaldehyde wt. % between about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2. In some embodiments, the feed to BPL purification system has a succinic anhydride wt. % between about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2. In some embodiments, the feed to BPL purification system has an EO wt% between about 0-3, about 0.5-2, about 1-2, about 1.4, at most about 1.4, or at most about 2. In some embodiments, the feed to the BPL purification system has trace amounts of carbonylation catalyst. In some embodiments, the feed to the BPL purification system has trace amounts of carbonylation catalyst components.

Evaporator

[0332] In some embodiments, the feed to the BPL purification system can be fed to evaporator **1628**. In some embodiments, the evaporator can operate at most about 5 bara, at most about 4 bara, at most about 3 bara, at most about 2 bara, at most about atmospheric pressure (i.e., 1 bara), or at about atmospheric pressure. In some embodiments, the evaporator can operate at a temperature between about 80-120°C, between about 90-100°C, between about 95-105°C, at about 100°C, at most about 100°C, at most about 105°C, at most about 110°C, or at most about 120°C. In some embodiments, the evaporator is a flash tank. Referring again to FIG. **16**, in the exemplary system evaporator **1628** can separate the feed into overhead stream **1629** and bottoms stream 1630. Overhead stream **1629** can comprise mainly of THF with low

boiling point components (e.g., CO, EO, acetaldehyde) and a small amount of bPL. In some embodiments, overhead stream **1629** can have a mass flow rate of at least about 9000 kg/hr, at least about 10000 kg/hr, at least about 11000 kg/hr, at least about 11500 kg/hr, or at least about 12000 kg/hr. In some embodiments, overhead stream 1629 can have a solvent (e.g., THF) wt% of about 75-95, about 80-90, about 85, about 86.7, at least about 75, at least about 80, at least about 85, or at least about 90. In some embodiments, overhead stream 1629 can have a bPL wt% of about 0-20, about 5-20, about 8-15, about 10, about 11.5, at most about 25, at most about 20, at most about 15, at most about 11.5, at most about 10, or at most about 5. In some embodiments, overhead stream 1629 can have a carbon monoxide wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.2, or at most about 0.1. In some embodiments, overhead stream 1629 can have an ethylene oxide wt% of about 0-5, about 0.5-3, about 1-2, about 1.6, at most 5, at most 3, at most 2, at most 1.6. In some embodiments, overhead stream 1629 can have an acetaldehyde wt% of about 0-0.4, about 0.1-0.3, about 0.2, at most about 0.4, or at most about 0.2.

[0333] In some embodiments, bottoms stream **1630** can have a mass flow rate of at least about 500 kg/hr, at least about 1000 kg/hr, at least about 1500 kg/hr, at least about 2000 kg/hr, at least about 2200 kg/hr, at least about 3000 kg/hr, at least about 4000 kg/hr, at least about 5000 kg/hr, at least about 10000 kg/hr, at least about 15000 kg/hr, at least about 20000 kg/hr, at least about 22000 kg/hr, at least about 30000 kg/hr. In some embodiments, bottoms stream 1630 can have a mass flow rate of between about 500 kg/hr and about 3000 kg/hr, between about 1000 kg/hr and about 3000 kg/hr, between about 1500 kg/hr and about 3000 kg/hr, between about 2000 kg/hr and about 3000 kg/hr, between about 2200 kg/hr and about 3000 kg/hr, between about 500 kg/hr and about 30000 kg/hr, between about 1000 kg/hr and about 30000 kg/hr, between about 1500 kg/hr and about 30000 kg/hr, between about 2000 kg/hr and about 30000 kg/hr, between about 2200 kg/hr and about 30000 kg/hr, between about 3000

kg/hr and about 30000 kg/hr, between about 4000 kg/hr and about 30000 kg/hr, between about 5000 kg/hr and about 30000 kg/hr, between about 10000 kg/hr and about 30000 kg/hr, between about 15000 kg/hr and about 30000 kg/hr, between about 20000 kg/hr and about 30000 kg/hr, between about 22000 kg/hr and about 30000 kg/hr. In some embodiments, bottoms stream 1630 can have a bPL wt% of about 60-95, about 65-90, about 70-85, about 75-85, about 79.7, about 80, at least about 65, at least about 70, at least about 75, at least about 79.7, at least about 85. In some embodiments, bottoms stream 1630 can have a solvent wt% of about 5-40, about 10-30, about 15-25, about 18-20, about 19.2, about 20, at most 40, at most 30, at most 25, at most 20, at most 19.2, at most 15, or at most 10. In some embodiments, bottoms stream 1630 can have an ethylene oxide wt% of about 0-0.4, about 0.1-0.3, about 0.2, at most about 0.4, or at most about 0.2. In some embodiments, bottoms stream 1630 can have a succinic anhydride wt% of about 0-2, about 0.2-1.6, about 0.4-1.2, about 0.6-1, about 0.7-0.9, at most about 2, at most about 1, at most about 0.8. In some embodiments, the bottoms stream 1630 can have a carbonylation catalyst wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.2, or at most about 0.1. In some embodiments, the bottoms stream 1630 can have a carbonylation catalyst component wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.2, or at most about 0.1.

Solvent Purification Column

[0334] Referring again to FIG. **16**, in the exemplary system depicted overhead stream **1629** can be sent to solvent purification column **1631**. The solvent purification column can be a distillation column. In some embodiments, the solvent purification column can be a stripping column or stripper. In some embodiments, the solvent purification column can operate at most about 5 bara, at most about 4 bara, at most about 3 bara, at most about 2 bara, at most about atmospheric pressure (i.e., 1 bara), or at about atmospheric pressure. In some embodiments, the evaporator can operate at a temperature of at most about 100°C, at most about 105°C, at

most about 110°C, or at most about 120°C. In some embodiments, an overhead temperature is maintained at about 20-60°C, about 30-50°C, about 40-50°C, about 44°C. In some embodiments, the solvent purification column can prevent bPL from getting into any vent streams. In some embodiments, solvent purification column can have at least 12 stages with a condenser as stage 1. In some embodiments, solvent purification column can have an internal cooler which can create a side stream. In some embodiments, solvent purification column can have an internal cooler above the side stream withdrawal. In some embodiments, internal cooler can be between stages in the middle of the column. In some embodiments, internal cooler can be between stages 5 and 6 of the solvent purification column. In some embodiments, solvent purification column can separate overhead stream **1629** into overhead stream **1632**, bottoms stream **1634**, and side stream **1633**. Overhead stream **1632** can comprise low boiling components (e.g., EO, CO, acetaldehyde) and around half solvent. Bottoms stream **1634** can comprise mainly bPL and solvent. In some embodiments, solvent purification column can recover at least 90wt%, at least 95wt%, at least 98wt%, at least 99wt%, or at least 99.5wt% of bPL from overhead stream 1629 in bottoms stream 1634.

[0335] In some embodiments, overhead stream **1632** can have a mass flowrate of at least 200 kg/hr, at least 300 kg/hr, at least 400 kg/hr, at least 411 kg/hr, at least 500 kg/hr, at least 1000 kg/hr, at least 1500 kg/hr, at least 2000 kg/hr, at least 3000 kg/hr, at least 4000 kg/hr, at least 4110 kg/hr, or at least 5000 kg/hr. In some embodiments, overhead stream **1632** can have a mass flowrate of between 200 kg/hr and 500 kg/hr, between 300 kg/hr and 500 kg/hr, between 400 kg/hr and 500 kg/hr, between 411 kg/hr and 500 kgr/hr, between 200 kg/hr and 5000 kg/hr, between 300 kg/hr and 5000 kg/hr, between 400 kg/hr and 5000 kg/hr, between 411 kg/hr and 5000 kgr/hr. In some embodiments, overhead stream 1632 can have a solvent (e.g., THF) wt% of about 30-70, about 40-60, about 45-55, about 50-55, about 50, about 53.9, at most 75, at most 65, at most 60, at most 55, at most 53.9, at most 50, at most 45. In some embodiments,

overhead stream 1632 can have an ethylene oxide wt% of about 20-60, about 30-50, about 35-45, about 37-43, about 40.6, at least about 20, at least about 25, at least about 30, at least about 35, at least about 40, at least about 40.6, at least about 45, or at least about 50. In some embodiments, overhead stream 1632 can have a carbon monoxide wt% of about 0-5, about 0.5-3, about 1-2, about 1.5-2, about 1.7, at most about 5, at most about 3, at most about 2, at most about 1.7, at most about 1. In some embodiments, overhead stream 1632 can have a acetaldehyde wt% of about 0-10, about 1-7, about 2-5, about 3-4.5, about 3.5-4, about 3.8, at most about 10, at most about 7, at most about 5, at most about 4, at most about 3.8, at most about 3.

[0336] In some embodiments, bottoms stream **1634** can have a mass flowrate of at least about 1000 kg/hr, at least about 1200 kg/hr, at least about 1400 kg/hr, at least about 1600 kg/hr, at least about 1643 kg/hr, at least about 1800 kg/hr, at least about 4000 kg/hr, at least about 7500 kg/hr, at least about 10000 kg/hr, at least about 12000 kg/hr, at least about 14000 kg/hr, at least about 16000 kg/hr, at least about 16430 kg/hr, or at least about 18000 kg/hr. In some embodiments, bottoms stream 1634 can have a mass flowrate of about 1000 kg/hr, about 1200 kg/hr, about 1400 kg/hr, about 1600 kg/hr, about 1643 kg/hr, about 1800 kg/hr, about 4000 kg/hr, about 7500 kg/hr, about 10000 kg/hr, about 12000 kg/hr, about 14000 kg/hr, about 16000 kg/hr, about 16430 kg/hr, or about 18000 kg/hr. In some embodiments, bottoms stream 1634 can have a mass flowrate of between 1000 kg/hr and 1800 kg/hr, between 1200 kg/hr and 1800 kg/hr, between 1400 kg/hr and 1800 kg/hr, between 1600 kg/hr and 1800 kg/hr, between 1643 kg/hr and 1800 kg/hr, between 1000 kg/hr and 18000 kg/hr, between 1200 kg/hr and 18000 kg/hr, between 14000 kg/hr and 18000 kg/hr, between 16000 kg/hr and 18000 kg/hr, between 1643 kg/hr and 18000 kg/hr, between 4000 kg/hr and 18000 kg/hr, between 10000 kg/hr and 18000 kg/hr, or between 16000 kg/hr and 18000 kg/hr. In some embodiments, bottoms stream 1634 can have a bPL wt% of about 60-95, about 70-90, about 75-85, about 80, about 80.4, at

least 60, at least 70, at least 75, at least 80, at least 80.4, at least 85, at least 90, or at least 95. In some embodiments, bottoms stream 1634 can have a solvent wt% of about 5-40, about 10-30, about 15-25, about 20, about 19.5, at most 40, at most 30, at most 25, at most 20, at most 19.5, at most 15, or at most 10. In some embodiments, bottoms stream 1634 can have an ethylene oxide wt% of about 0-0.4, about 0.1-0.3, about 0.2, at most about 0.4, or at most about 0.2.

[0337] In some embodiments, side stream **1633** can have a mass flow rate of at least about 6000 kg/hr, at least about 7000 kg/hr, at least about 8000 kg/hr, at least about 9000 kg/hr, at least about 9500 kg/hr, at least about 9508 kg/hr, at least about 10000 kg/hr, at least about 20000 kg/hr, at least about 40000 kg/hr, at least about 60000 kg/hr, at least about 70000 kg/hr, at least about 80000 kg/hr, at least about 90000 kg/hr, at least about 95000 kg/hr, at least about 95080 kg/hr, or at least about 100000 kg/hr. In some embodiments, side stream 1633 can have a mass flow rate of about 6000 kg/hr, about 7000 kg/hr, about 8000 kg/hr, about 9000 kg/hr, about 9500 kg/hr, about 9508 kg/hr, about 10000 kg/hr, about 20000 kg/hr, about 40000 kg/hr, about 60000 kg/hr, about 70000 kg/hr, about 80000 kg/hr, about 90000 kg/hr, about 95000 kg/hr, about 95080 kg/hr, or about 100000 kg/hr. In some embodiments, side stream 1633 can have a mass flow rate of between 6000 kg/hr and 10000 kg/hr, between 7000 kg/hr and 10000 kg/hr, between 8000 kg/hr and 10000 kg/hr, between 9000 kg/hr and 10000 kg/hr, between 9500 kg/hr and 10000 kg/hr, between 9508 kg/hr and 10000 kg/hr, between 6000 kg/hr and 100000 kg/hr, between 10000 kg/hr and 100000 kg/hr, between 20000 kg/hr and 100000 kg/hr, between 40000 kg/hr and 100000 kg/hr, between 60000 kg/hr and 100000 kg/hr, between 70000 kg/hr and 100000 kg/hr, between 80000 kg/hr and 100000 kg/hr, or between 90000 kg/hr and 100000 kg/hr, between. In some embodiments, side stream 1633 can have a solvent wt% of at least 95, at least 98, at least 99, at least 99.7. In some embodiments, side stream 1633 can have an ethylene oxide wt. % of about 0-0.4, about 0.1-0.3, about 0.2, at most about

0.4, or at most about 0.2. In some embodiments, side stream 1633 can have a bPL wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2.

BPL Purification Column

[0338] Bottoms stream **1630** and bottoms stream **1634** can be combined and sent to BPL purification column **1635**. BPL purification column can be a distillation column. In some embodiments, BPL purification column can be a vacuum column or a column operating under reduced pressure. In some embodiments, the operating pressure of the BPL purification column can be less than atmospheric pressure (1 bara), less than about 0.5 bara, less than about 0.25 bara less than 0.2 bara, less than 0.15 bara, or about 0.15 bara. In some embodiments, the BPL purification column can include a reboiler that can be maintained at most about 120°C, at most about 110°C, at most about 100°C, or about 100°C. In some embodiments, an overhead temperature is maintained at about 5-30°C, about 10-20°C, about 12-16°C, about 14°C.

[0339] In some embodiments, BPL purification column can separate the combined bottoms streams **1630** and **1634** into overhead stream **1636** and bottoms stream 1618 (i.e., BPL purified stream **1618**). Bottoms stream **1618** can be substantially pure bPL with minimal solvent. In some embodiments, bottoms stream **1618** can also include some heavy components such as residual carbonylation catalyst and succinic anhydride. The carbonylation catalyst can be considered to be non-volatile and can accumulate in the BPL purification column's sump. Accumulated catalyst can be removed periodically by purging sump when the catalyst wt% reaches a predefined value (e.g., at least 1wt%, 2wt%, 3wt%, 4wt%, or 5wt%). In contrast to the carbonylation catalyst, succinic anhydride can have some volatility and if accumulated in the sump can produce an undesirable rise in boiling temperature in the reboiler. In some embodiments, succinic anhydride can also accumulate in the sump and can be purged in the same manner the accumulated catalyst can be purged. In some embodiments, overhead stream 1636 can have a mass flow rate of about at least about 500 kg/hr, at least about 600 kg/hr, at

least about 700 kg/hr, at least about 750 kg/hr at least about 800 kg/hr, or at least about 850 kg/hr. In some embodiments, overhead stream 1636 can have a solvent wt% of at least about 95, at least about 98, at least about 99, at least about 99.1, or at least about 99.5. In some embodiments, overhead stream 1636 can have an ethylene oxide wt% of about 0-3, about 0.2-2, about 0.2-1.5, about 0.5-1, about 0.8, at most about 3, at most about 2, at most about 1, at most about 0.8, at most about 0.5. In some embodiments, overhead stream 1638 can have an acetaldehyde wt% of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2.

[0340] In some embodiments, bottoms stream **1618** can have a mass flow rate of at least about 1000 kg/hr, at least about 2000 kg/hr, at least about 2500 kg/hr, at least about 3000 kg/hr, at least about 3100 kg/hr, at least about 3500 kg/hr, at least about 4000 kg/hr, at least about 5000 kg/hr, at least about 1000 kg/hr, at least about 20000 kg/hr, at least about 35000 kg/hr, at least about 36380 kg/hr, or at least about 40000 kg/hr. In some embodiments, bottoms stream 1618 can have a mass flow rate of about 2000 kg/hr, about 2500 kg/hr, about 3000 kg/hr, about 3500 kg/hr, about 3638 kg/hr, about 4000 kg/hr, about 5000 kg/hr, about 1000 kg/hr, about 20000 kg/hr, about 35000 kg/hr, about 36380 kg/hr, or about 40000 kg/hr. In some embodiments, bottoms stream 1618 can have a mass flow rate of between 1000 kg/hr and 4000 kg/hr, or between 1000 kg/hr and 40000 kg/hr. In some embodiments, bottoms stream 1618 can have a bPL wt% of at least about 95, at least about 98, at least about 99, at least about 99.3, or at least about 99.5. In some embodiments, bottoms stream 1618 can have a solvent wt. % of about 0-0.2, about 0.05-0.15, about 0.1, at most about 0.1, or at most about 0.2. In some embodiments, bottoms stream 1618 can have a succinic anhydride wt% of about 0-3, about 0.1-2, about 0.2-1, about 0.5-1, about 0.6, at most about 3, at most about 2, at most about 1, at most about 0.6, at most about 0.5. In some embodiments, bottoms stream 1618 can have trace amounts of carbonylation catalyst. In some embodiments, BPL purification column can have

a purge for the carbonylation catalyst and/or succinic anhydride in the bottoms stream **1618**. In some embodiments, the purge can be a valve.

Light Gas Column

[0341] Overhead stream **1632** can be sent to light gas column **1637** to be separated into overhead stream **1639** and bottoms stream **1638**. The light gas column can be a distillation column. In some embodiments, the light gas column can operate at most about 5 bara, at most about 4 bara, at most about 3 bara, at most about 2 bara, at most about atmospheric pressure (i.e., 1 bara), or at about atmospheric pressure. In some embodiments, light gas column can include a partial condenser. In some embodiments, the partial condenser operates at a temperature of at about 0-20°C, about 5-15°C, about 10-15 °C, about 10-13 °C. In some embodiments, the temperature maintained at the bottom of light gas column is about 20-70°C, about 40-60°C, about 45-55°C, or about 50°C. In some embodiments, the overhead temperature maintained in light gas column can be about -10-10°C, about -5-5°C, about -2-3°C, or about 1 °C. Overhead stream 1639 can comprise mostly of the acetaldehyde produced in the carbonylation reaction system as well as low boiling point ethylene oxide. In some embodiments, overhead stream 1639 can be disposed of (e.g., incinerator, flare, etc.) so acetaldehyde does not accumulate in the overall production system/production process.

[0342] In some embodiments, overhead stream **1639** can have a mass flow rate of about 50 kg/hr, about 100 kg/hr, about 150 kg/hr, about 175 kg/hr, about 200 kg/hr, about 250 kg/hr, at least 500 kg/hr, at least 1000 kg/hr, at least 1500 kg/hr, at least 2000 kg/hr, or at least 2500 kg/hr. In some embodiments, overhead stream 1639 can have a mass flow rate of between 50 kg/hr and 250 kg/hr, between 100 kg/hr and 250 kg/hr, between 200 kg/hr and 250 kg/hr, or between 50 kg/hr and 2000 kg/hr. In some embodiments, overhead stream 1639 can have an ethylene oxide wt% of at least about 70, at least about 75, at least about 80, at least about 85, at least about 89.5, at least about 90, or at least about 95. In some embodiments, overhead

stream 1639 can have an acetaldehyde wt% of about 0-15, about 1-10, about 2-8, about 6.1, at most about 15, at most about 10, at most about 6.1, at most about 5, or at most about 2. In some embodiments, overhead stream 1639 can have a carbon monoxide wt% of about 0-12, about 1-10, about 2-6, about 4.10, at most about 12, at most about 10, at most about 6, at most about 5, at most about 4.1, or at most about 2. In some embodiments, overhead stream 1639 can have a solvent wt. % of about 0-2, about 0.1-1, about 0.2-0.6, about 0.4, at most about 2, at most about 1, at most about 0.5, at most about 0.4, or at most about 0.2.

[0343] In some embodiments, bottoms stream **1638** can have a mass flow rate of about 50 kg/hr, about 150 kg/hr, about 200 kg/hr, about 235 kg/hr, about 250 kg/hr, about 300 kg/hr or about 350 kg/hr. In some embodiments, bottoms stream 1638 has a solvent wt% of at least about 75, at least about 80, at least about 85, at least about 90, at least about 93.9, at least about 95, at least about 98, or at least about 99. In some embodiments, bottoms stream 1638 has an ethylene oxide wt% of about 0-12, about 1-10, about 2-6, about 4, at most about 12, at most about 10, at most about 8, at most about 5, at most about 4, or at most about 2. In some embodiments, bottoms stream 1638 has an acetaldehyde wt% of about 0-10, about 0.5-5, about 1-4, about 1-3, about 2.2, at most about 10, at most about 5, at most about 2.2, at most about 2, at most about 1.

Solvent Recycle Stream

[0344] In some embodiments, side stream **1633**, bottoms stream **1638**, overhead stream **1636** or combinations thereof can form solvent recycle stream **1623**. In some embodiments, side stream **1633**, bottoms stream **1638**, and overhead stream **1636** can be combined to form solvent recycle stream **1623**. In some embodiment, side stream **1633**, bottoms stream **1638**, and/or overhead stream **1636** can be sent to a solvent recycle tank or storage. In some embodiments, the solvent recycle stream is fed back to the carbonylation reaction system. In some embodiments, the solvent recycle stream fed to the carbonylation reaction system is from

the solvent recycle tank or storage. In some embodiments, the solvent streams entering and/or exiting the solvent recycle tank or storage can be purified for example by passing the stream through an absorber to remove potential oxygen and/or moisture from the stream. In some embodiments, the solvent recycle tank or storage can be equipped with sensors to determine the water and/or oxygen content in the storage tank.

Preferred Distillation System

[0345] In preferred embodiment, distillation sub-system consists of 3 distillation columns: (1) Lights Removal column, (2) THF Solvent Recovery column, and (3) bPL Purification column.

1. Lights Revmoval Column

[0346] The purpose of this column is to recover Ethylene Oxide (EO) for recycle back to the Carbonylation Reactor as well as to separate low-boiling impurities such as Acetaldehyde (ACH). Distillate stream from this column may contain THF, EO, ACH or only EO and ACH. This colomn receives a permeate stream from a carbonylation catalyst recovery zone and in a highly preferred form has the following component with representativie compositions of THF (about 75.2 wt%), bPL (about 20.5wt%), Ethylene Oxide (about 4.1wt%), Acetaldehyde (about 0.07wt%), Succinic Anhydride (about 0.02wt%), traces of low and high boiling impurities, and trace residual carbonylation catalyst is fed to Lights Removal distillation column. The distillation column is operated at the pressure of about 1.3 bara (column is operated at atmospheric pressure or slightly above atmospheric pressure). The reboiler temperature is maintained at or below 105°C. Lights column distillate stream consisting essentially of THF (about 93.4wt%), EO (about 6.5wt%), ACH (0.1wt%), and traces of low boiling impurities is fed back to the carbonylation reactor or to optional ACH removal system. The lights column in a a highly preferred form produces a bottoms stream consisting essentially of bPL (about 54.9wt%), THF (about 45.0wt%), Succinic Anhydride (about 0.05wt%), trace amounts of low-

and high-boiling impurities, and trace residual carbonylation catalyst and high-boiling impurities is fed forward to THF Solvent Recovery column (2).

[0347] In some embodiments Lights Removal column can be operated in such a way that Distillate stream consists of only Ethylene Oxide and Acetaldehyde and all THF is exiting the column with the Bottoms stream. If the lights removal column is operated in this configuration the distillate consists essentially of EO (about 98.8wt%), ACH (about 1.2wt%), and trace of low boiling impurities. The bottoms stream in this column configuration consists essentially of THF (about 78.5wt%), bPL (about 21.5wt%), SAH (about 0.02wt%), trace amounts of residual carbonylation catalyst, trace amounts of low- and high-boiling impurities.

[0348] Accumulation of Acetaldehyde within carbonylation/distillation system can be avoided by implementing a small purge from distillate stream or removed from the distillate stream using an absorbent such as molecular sieves (non-limiting examples are Molecular Sieve 3A, 4A, 5A, 13X, etc.). Optionally, ACH is separated from EO using distillation or extractive distillation.

2. THF Solvent Recovery Column

[0349] The purpose of this column is to recover THF solvent for recycle back to the carbonylation reactor. Due to the high boiling point of bPL (162°C at atmospheric pressure) this column is operated at pressures below atmospheric to limit the reboiler temperature below 105°C and avoid autopolymerization of bPL. Distillate stream from this column contains essentially pure THF and bottoms stream of this column contains bPL, SAH, residual carbonylation catalyst, and trace amounts of high boiling impurities.

[0350] Lights Column Bottom stream containing THF, bPL, SAH, residual carbonylation catalyst, and trace amounts of low and high boiling impurities is fed to THF Solvent Recovery distillation column (the composition of this stream is presented in the section above).

Optionally, the THF solvent make-up stream may be fed to this column – this allows removal of O2, H2O, and BHT inhibitor from make-up THF.

[0351] The distillation column is operated at the absolute pressure of about 100 Torrs (column is operated under vacuum) and the reboiler temperature is maintained at or below 105°C. The column is designed to minimize air intrusion into the column simplifying removal of O2 and H2O contaminants from recycled THF Solvent stream in downstream unit operation.

[0352] The distillate stream from this column consisting of essentially pure THF (purity greater than 99.9wt%) with trace amounts of low- and high-boiling impurities is recycled back to the carbonylation reactor. Optionally and before it is recycled, this stream may be passed through purification system for removal of contaminants such as O2 and H2O. These impurities can be removed by any means known in the art such as absorption, adsorption, extractive distillation, azeotropic distillation, etc.

[0353] The bottoms stream consists of bPL (about 99.8wt%), SAH (about 0.1 wt%), small amounts of residual carbonylation catalyst, and traces of low- and high-boiling impurities. This stream is fed forward to bPL Purification column.

3. bPL Purification Column

[0354] The purpose of this column is to recover purified bPL for subsequent production of PPL (poly-propiolactone). Due to high boiling point of bPL (162°C at atmospheric pressure) this column is operated at pressures below atmospheric to limit the reboiler temperature below 105°C and avoid autopolymerization of bPL. The distillate stream from this column contains essentially pure bPL. The bottoms stream of this column contains residual bPL, SAH, residual carbonylation catalyst, and trace amounts of high boiling impurities. The Purified bPL stream is fed forward to Polymerization Reactor and bottoms stream is sent for disposal or recovery of residual bPL and SAH. The bottoms stream from THF recovery column containing bPL

(about 99.8wt%), SAH (about 0.1 wt%), residual carbonylation catalyst, and traces of low- and high-boiling impurities is fed to bPL Purification column.

[0355] The bPL purification column is in preferred form operated at the absolute pressure of about 60 Torrs (column is operated under vacuum) and the reboiler temperature is maintained at or below 105°C. The distillate stream consisting of essentially pure bPL (purity greater than 99.9wt%) with trace amounts of low- and high-boiling impurities is fed forward to bPL Polymerization reactor.

[0356] The Bottoms stream of this column consists of bPL (about 88.9wt%), SAH (about 9.7wt%), carbonylation catalyst (about 1.4wt%), and trace high-boiling impurities. The amount of bPL in this bottoms stream is selected to avoid crystallization of SAH at the temperatures below its melting point of 119°C and to limit the reboiler temperature to below 105°C.

Polypropiolactone Production system/production process

[0357] With reference to FIG. **2**, the relationship of the polypropiolactone production system/production process with other unit operations, such as the β-propiolactone purification system, the ion removal unit, and the glacial acrylic acid production system/production process, is depicted.

[0358] β-Propiolactone purification system **202** is configured to feed a β-propiolactone product stream into polypropiolactone production system/production process **210**. Homogeneous catalyst delivery system **204** is configured to feed a homogeneous polymerization catalyst into the polymerization reactor of polypropiolactone production system/production process **210**. Polypropiolactone production system/production process **210** is configured to polymerize β-propiolactone to produce polypropiolactone. Depending on the type of polymerization reactors selected and the configuration of such reactors, as well as the operating conditions (*e.g.*, operating temperature, operating pressure, and residence time) and

choice of polymerization catalysts used, the extent of conversion of the β-propiolactone may be controlled. In some variations, operating temperature is the average temperature of the contents of the reactor.

[0359] In some variations, partial conversion of β-propiolactone to polypropiolactone is achieved, and bPL recycle unit **220** is configured to recycle at least a portion of unreacted β-propiolactone to polypropiolactone production system/production process **210**. In other variations, complete conversion of β-propiolactone to polypropiolactone is achieved. The polypropiolactone product stream produced from polypropiolactone production system/production process **210** is fed glacial acrylic acid production system/production process **250**, which is configured to produce glacial acrylic acid from the polypropiolactone. Ion removal units **230** and **260** are present to remove at cationic and/or anionic carbonylation catalyst species that may be carried over from the upstream carbonylation reaction in the β-propiolactone production system/production process (not depicted in FIG. **2**). For example, when the carbonylation catalyst is a cobalt-aluminum compound, cobalt and aluminum species may be removed by ion removal units **230** and **260**. The ionic species isolated by the ion removal units may be disposed using unit **270**, or regenerated in unit **280** to produce an active carbonylation catalyst that may be recycled into the β-propiolactone production system/production process.

[0360] In some variations, unit **240** is configured to receive the polypropiolactone product stream (*e.g.*, in liquid form) from polypropiolactone production system/production process **210**, and is configured to pelletize, extrude, flake, or granulate the polypropiolactone product stream.

[0361] It should be understood, however, that FIG. **2** provides one exemplary configuration of these unit operations. In other variations, one or more of the unit operations depicted in FIG.

2 may be added, combined or omitted, and the order of the unit operations may be varied as well.

[0362] With reference again to FIG. 1, the polypropiolactone production system/production process is configured to produce polypropiolactone by polymerizing β-propiolactone in the presence of a polymerization catalyst. While FIG. **1** depicts the use of a single plug flow reactor for the polymerization of β-propiolactone to produce polypropiolactone, other reactor types and reactor configurations may be employed.

[0363] In some embodiments, the polypropiolactone production system/production process includes a β-propiolactone, a polymerization initiator or catalyst source, and at least one polymerization reactor.

BPL Source

[0364] With reference again to FIGS. **6-13**, the bPL entering the polypropiolactone production system/production process may be purified bPL from the bPL purification train or recycled bPL from the polymerization reactor, or a combination thereof.

[0365] In some embodiments, the inlet to the polymerization process can include at least about 2000 kg/hr bPL, at least about 2500 kg/hr bPL, at least about 3000 kg/hr bPL, at least about 3086 kg/hr bPL, at least about 3500 kg/hr bPL, at least about 3638 kg/hr bPL, at least about 4000 kg/hr bPL, at least about 5000 kg/hr bPL, at least about 1000 kg/hr bPL, at least about 20000 kg/hr bPL, or at least about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include about 2000 kg/hr bPL, about 2500 kg/hr bPL, about 3000 kg/hr bPL, about 3500 kg/hr bPL, about 3638 kg/hr bPL, about 4000 kg/hr bPL, about 5000 kg/hr bPL, about 1000 kg/hr bPL, about 20000 kg/hr bPL, or about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include between about 2000 kg/hr bPL and about 3500 kg/hr bPL, between about 2500 kg/hr bPL and about 3500 kg/hr bPL, between about 3000 kg/hr bPL and about 3500 kg/hr bPL, between about 2000 kg/hr bPL

and about 35000 kg/hr bPL, between about 2500 kg/hr bPL and about 35000 kg/hr bPL, or between about 3000 kg/hr bPL and about 35000 kg/hr bPL. In some embodiments, the inlet to the polymerization process can include at least about 25 kmol/hr bPL, at least about 30 kmol/hr bPL, at least about 40 kmol/hr bPL, at least about 42 kmol/hr bPL, or at least about 50 kmol/hr bPL. In some embodiments, the mass fraction of bPL in the inlet to the polymerization process can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.99, and at least about 0.993. In some embodiments, the mole fraction of bPL in the inlet to the polymerization process can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.99, and at least about 0.995. The remainder of the production stream entering the polymerization process can include secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.015, at most about 0.01, or at most about 0.004) and left over solvent (e.g., THF) and leftover carbonylation catalyst (in at most about 1000 ppm). In some variations, the remainder of the production stream entering the polymerization process can include carbonylation catalyst components (in at most about 1000 ppm).

[0366] In some variations, the production stream entering the polymerization process further comprises other compounds, such as carbonylation catalyst or components thereof. For example, in some embodiments, the production stream further comprises cobalt or aluminum, or a combination thereof, from the carbonylation catalyst.

[0367] Carbonylation catalyst components may include, for example, compounds produced by degradation of the catalyst, compounds used to produce the catalyst, metals or metal ions which were part of the catalyst, any organic compounds which were part of the catalyst, metal carbonyls or metal complexes which were part of the catalyst. For example, in some embodiments, carbonylation catalyst components are carbonyl cobaltate, aluminum salen

compounds, aluminum porphyrin compounds, aluminum salophen compounds, cobalt or cobalt ions, or aluminum or aluminum ions, or any combinations thereof.

[0368] In certain variations, the production stream entering the polymerization process comprises cobalt. In some embodiments, the cobalt is Co^{-1}, Co, Co^{+}, Co^{2+}, or Co^{3+}, or a combination thereof. In some embodiments, the production stream has a cobalt concentration between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM and 0.015 mM.

[0369] In certain variations, the production stream entering the polymerization process comprises aluminum. In some embodiments, the concentration of aluminum in the production stream is between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM and 0.015 mM. In certain variations, the production stream entering the polymerization process contains less than 1ppm cobalt and less than 1ppm aluminum.

[0370] In some embodiments, the inlet to the polymerization process can also include a polymerization catalyst, for example, if the polymerization reaction is a homogenous polymerization reaction. The production stream entering the polymerization process can be the heavy (i.e., bottoms) stream from the BPL Purification system (e.g., BPL distillation system). In some embodiments, the production stream entering the polymerization process can have a temperature between about 30-120°C, between about 50-110°C, or about 70°C. In some embodiments, the production stream entering the polymerization process can be at a pressure of at least about 0.05 bar, at least about 0.1 bar, at least about 5 bar, at least about 10 bar, at least about 15 bar, or at least about 20 bar. In some embodiments, production stream entering the polymerization process is between 0.05 bar and 20 bar, between 0.1 bar and 20 bar, between 5 bar and 15 bar, or between 10 bar and 20 bar.

[0371] In some variations, the mole ratio of bPL feed rate to the polymerization initiaor feed rate entering the polymerization process is from 500 to 20,000, from 1,000 to 10,000, from 2,000 to 9,000, from 3,000 to 8,000, from 5,000 to 7,000, from 1,000 to 110,000, from 5,000 to 110,000, from 25,000 to 110,000, from 50,000 to 110,000, or from 75,000 to 110,000. In one embodiment, mole ratio of bPL feed rate to the polymerization catalyst feed rate entering the polymerization process is from 1,000 to 9,000.

[0372] In some variations, bPL from the bPL purification process and bPL recycled from the polymerization process both enter the polymerization process. In certain embodiments, the weight ratio of recycled bPL to bPL from the bPL Purification process is from 0 to 0.01:0.99, from 0.4:0.6 to 0.1:0.9, from 0.5:0.5 to 0.15:0.85, from 0.35:0.65 to 0.1:0.9, or from 0.25:0.75 to 0.15:0.85.

Other Feed Sources

[0373] The polymerization process may further include other feed sources. For example, in one variation, the polymerization system further includes a polymerization initiator source, and the reactor is configured to receive a polymerization initiator from such source. In some variations, the polymerization initiator is a nucleophile.

Polymerization Conditions

[0374] In certain embodiments, conversion of bPL to PPL is performed in a continuous flow format. In certain embodiments, conversion of bPL to PPL is performed in a continuous flow format in the gas phase. In certain embodiments, conversion of bPL to PPL is performed in a continuous flow format in the liquid phase. In certain embodiments, conversion of bPL to PPL is performed in a liquid phase in a batch or semi-batch format. Conversion of bPL to PPL may be performed under a variety of conditions. In certain embodiments, the reaction may be performed in the presence of one or more catalysts that facilitate the transformation of the bPL to PPL.

[0375] In some embodiments, the production stream entering the polymerization process is a gas or a liquid. The conversion of bPL to PPL in the polymerization process may be performed in either the gas phase or the liquid phase and may be performed neat, or in the presence of a carrier gas, solvent, or other diluent.

[0376] In certain variations, the operating temperature of the polymerization reactor is maintained at or below the pyrolysis temperature of polypropiolactone. In some embodiments, the temperature of the reaction zone is maintained at or below about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 0 °C to about 200 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 25 °C to about 200 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 50 °C to about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 70 °C to about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 100 °C to about 150 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 0 °C to about 100 °C. In some embodiments, the operating temperature of the polymerization reactor is maintained at about 50 °C to about 100 °C. In some variations, operating temperature is the average temperature of the contents of the reactor.

[0377] In some variations, the polymerization reactor is configured to produce PPL with a residence time from 1 second to 10 hours, from 1 second to 3 hours, from 1 min to 2 hours, from 1.5 min to 90 min, from 2 min to 75 min, from 2 min to 60 min, from 2 min to 45 min, from 3 min to 30 min, or from 4 min to 15 min. In one embodiment the residence time of the reaction mixture is from 2 min to 90 min. In certain variations, residence time refers to the length of time a material spends in a vessel (for example, a reaction vessel). It may be

calculated by specifying the volumetric flow rate of material and active volume of the vessel which the material is contained.

[0378] In some variations, the polymerization reactor is configured to produce PPL at an operating pressure from 0.01 bar to 100 bar, from 0.01 bar to 50 bar, from 0.1 bar to 30 bar, from 1 bar to 20 bar, from 2 bar to 15 bar, from 3 bar to 10 bar, from 0.01 bar to 15 bar, from 0.01 bar to 10 bar, from 0.1 bar to 5 bar, or from 0.1 bar to 2 bar. In some embodiments, the polymerization reactor is a CSTR and operating pressure in the reactor is from 0.1 bar to 5 bar. In other embodiments, the polymerization reactor is a PFR and the operating pressure in the reactor is from 1 bar to about 20 bar. In still other embodiments, the polymerization reactor is a loop reactor and the operating pressure in the reactor is from 1 bar to about 20 bar.

Homogeneous Catalysts and Initiators

[0379] Any suitable polymerization initiators and/or catalysts may be used to convert the BPL product stream entering the PPL production system/production process into a PPL product stream. In some embodiments, the polymerization initiator or catalyst is homogenous with the polymerization reaction mixture. Any suitable homogeneous polymerization initiator or catalyst capable of converting the production stream to the PPL product stream may be used in the methods described herein.

[0380] Catalysts suitable for the ring-opening polymerization step of the methods disclosed herein are disclosed, for example, in: Journal of the American Chemical Society (2002), 124(51), 15239-15248 Macromolecules, vol. 24, No. 20, pp. 5732-5733, Journal of Polymer Science, Part A-1, vol. 9, No. 10, pp. 2775-2787; Inoue, S., Y. Tomoi, T. Tsuruta & J. Furukawa; Macromolecules, vol. 26, No. 20, pp. 5533-5534; Macromolecules, vol. 23, No. 13, pp. 3206-3212; Polymer Preprints (1999), 40(1), 508-509; Macromolecules, vol. 21, No. 9, pp. 2657-2668; and Journal of Organometallic Chemistry, vol. 341, No. 1-3, pp. 83-9; and in US

Patent Nos. 3,678,069, 3,169,945, 6,133,402; 5,648,452; 6,316,590; 6,538,101; and 6,608,170. The entirety of each of which is hereby incorporated herein by reference.

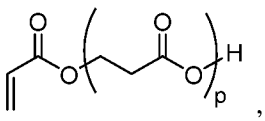
[0381] The polymerization process may further comprise a polymerization initiator including but not limited to amines, polyamines, phosphines amongst others. Further, a variety of polymerization initiators may be used in the polymerization process, including by not limited to -carbonates of alkali- and alkaline earth metals.

[0382] In certain embodiments, suitable polymerization – initiators include carboxylate salts of metal ions or organic cations.

[0383] In certain embodiments, a polymerization initiator is combined with the production stream containing bPL. In certain embodiments, the molar ratio of the polymerization initiator to the bPL in the production stream is about 1:15000. In certain embodiments, the molar ratio of polymerization intiator:bPL is about 1:100, 1:10000, 1:1000, 1:20000 or a range including any two of these ratios.

[0384] In certain embodiments, where the polymerization ~~catalyst~~ initiator comprises a carboxylate salt, the carboxylate has a structure such that upon initiating polymerization of bPL, the polymer chains produced have an acrylate chain end. In certain embodiments, the carboxylate ion on a polymerization initiator is the anionic form of a chain transfer agent used in the polymerization process.

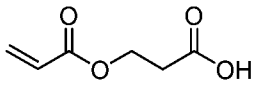
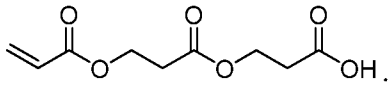
[0385] In certain embodiments, the carboxylate salt of the polymerization initiator is a salt of (i.e., the anionic form) a compound of Formula (**A**):



,

(**A**)

or a mixture of any two or more of these, where *p* is from 0 to 9. In certain embodiments, *p* is from 0 to 5. In certain embodiments, the carboxylate salt of the polymerization ~~catalyst~~ initiator is an acrylate salt (i.e. compound of Formula (**A**) where p = 0).

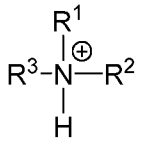
[0386] In certain embodiments, the carboxylate salt of the polymerization initiator is a salt of an acrylic acid dimer, . In certain embodiments, the carboxylate salt of the polymerization ~~catalyst~~ initiator is a salt of an acrylic acid trimer, .

[0387] In certain embodiments, where the polymerization initiator comprises a carboxylate salt, the carboxylate is the anionic form of a C_{1-40} carboxylic acid. In certain embodiments, the carboxylate salt can be a salt of a polycarboxylic acid (e.g. a compound having two or more carboxylic acid groups). In certain embodiments, the carboxylate comprises the anion of a C_{1-20} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of a C_{1-12} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of a C_{1-8} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of a C_{1-4} carboxylic acid. In certain embodiments, the carboxylate comprises the anion of an optionally substituted benzoic acid. In certain embodiments, the carboxylate is selected from the group consisting of: formate, acetate, propionate, valerate, butyrate, C_{5-10} aliphatic carboxylate, and C_{10-20} aliphatic carboxylate.

[0388] As noted, in certain embodiments, the polymerization initiator comprises a carboxylate salt of an organic cation. In certain embodiments, the polymerization initiator comprises a carboxylate salt of a cation wherein the positive charge is located at least partially on a nitrogen, sulfur, or phosphorus atom. In certain embodiments, the polymerization initiator comprises a carboxylate salt of a nitrogen cation. In certain embodiments, the polymerization initiator comprises a carboxylate salt of a cation selected from the group consisting of:

ammonium, amidinium, guanidinium, a cationic form of a nitrogen heterocycle, and any combination of two or more of these. In certain embodiments, the polymerization ~~catalyst~~ initiator comprises a carboxylate salt of a phosphorus cation. In certain embodiments, the polymerization ~~catalyst~~ initiator comprises a carboxylate salt of a cation selected from the group consisting of: phosphonium and phosphazenium. In certain embodiments, the polymerization ~~catalyst~~ initiator comprises a carboxylate salt of a sulfur-containing cation. In certain embodiments, the polymerization initiator comprises a sulfonium salt.

[0389] In certain embodiments, the polymerization initiator comprises a carboxylate salt of a protonated amine:



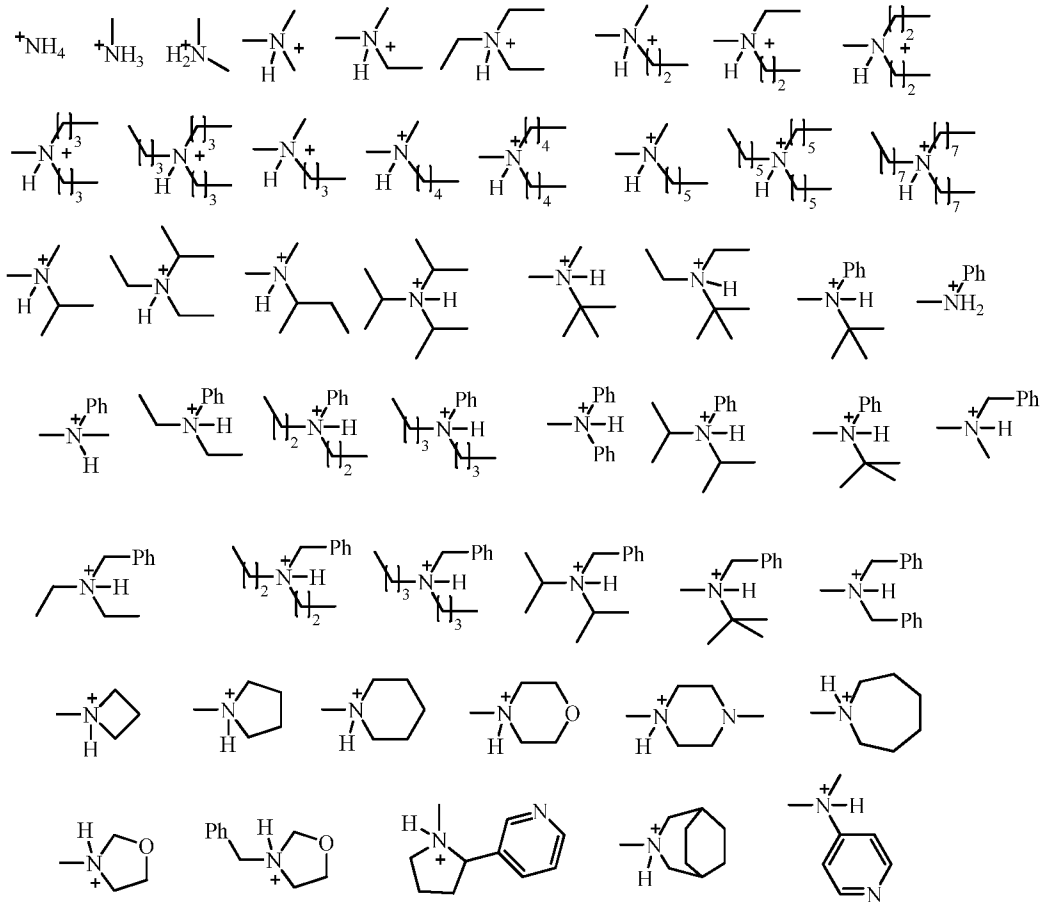
,

wherein:

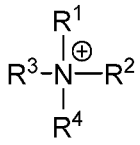
each R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7- to 14-membered saturated or partially unsaturated polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an 8- to 14-membered polycyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated monocyclic heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 14-membered saturated or partially unsaturated polycyclic heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; phenyl; or an 8- to 14-membered polycyclic aryl ring; wherein R^1 and R^2 can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; each R^3 is independently hydrogen or an optionally substituted radical

selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7- to 14-membered saturated or partially unsaturated polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an 8- to 14-membered polycyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated monocyclic heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 14-membered saturated or partially unsaturated polycyclic heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; phenyl; or an 8- to 14-membered polycyclic aryl ring; wherein an R^3 group can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

[0390] In certain embodiments where the polymerization initiator comprises a carboxylate salt of a protonated amine, the protonated amine is selected from the group consisting of:



[0391] In certain embodiments, the polymerization initiator comprises a carboxylate salt of a quaternary ammonium salt:

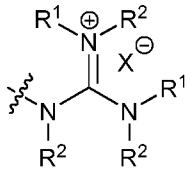


wherein:

each R^1, R^2 and R^3 is described above; and

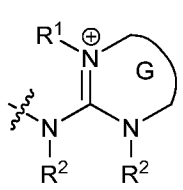
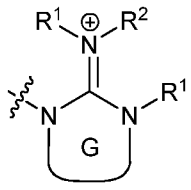
each R^4 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7- to 14-membered saturated or partially

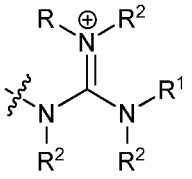
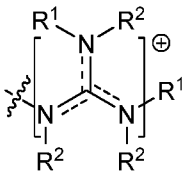
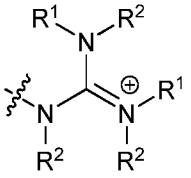
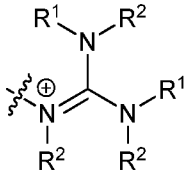
unsaturated polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an 8- to 14-membered polycyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated monocyclic heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 14-membered saturated or partially unsaturated polycyclic heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; phenyl; or an 8- to 14-membered polycyclic aryl ring; wherein an R^4 group can be taken with an R^1, R^2 or R^3 group to form one or more optionally substituted rings.

[0392] In certain embodiments, the polymerization initiator comprises a carboxylate salt of a guanidinium group: , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein. In certain embodiments, each R^1 and R^2 is independently hydrogen or C_{1-20} aliphatic. In certain embodiments, each R^1 and R^2 is independently hydrogen or C_{1-12} aliphatic. In certain embodiments, each R^1 and R^2 is independently hydrogen or C_{1-20} heteroaliphatic. In certain embodiments, each R^1 and R^2 is independently hydrogen or phenyl. In certain embodiments, each R^1 and R^2 is independently hydrogen or 8- to 10-membered aryl. In certain embodiments, each R^1 and R^2 is independently hydrogen or 5- to 10-membered heteroaryl. In certain embodiments, each R^1 and R^2 is independently hydrogen or 3- to 7-membered heterocyclic. In certain embodiments, one or more of R^1 and R^2 is optionally substituted C_{1-12} aliphatic.

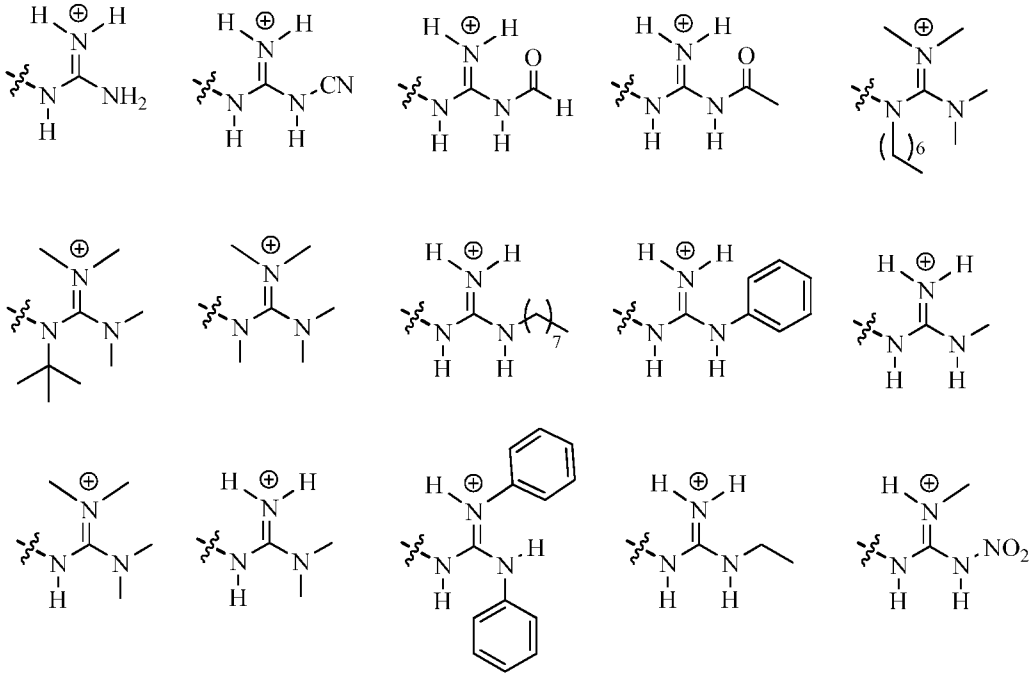
[0393] In certain embodiments, any two or more R^1 or R^2 groups are taken together with intervening atoms to form one or more optionally substituted carbocyclic, heterocyclic, aryl, or heteroaryl rings. In certain embodiments, R^1 and R^2 groups are taken together to form an

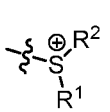
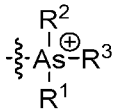
optionally substituted 5- or 6-membered ring. In certain embodiments, three or more R^1 and/or R^2 groups are taken together to form an optionally substituted fused ring system.

[0394] In certain embodiments, an R^1 and R^2 group are taken together with intervening atoms to form a compound selected from:  or , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein, and Ring G is an optionally substituted 5- to 7-membered saturated or partially unsaturated heterocyclic ring.

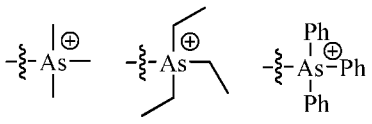
[0395] It will be appreciated that when a guanidinium cation is depicted as , all such resonance forms are contemplated and encompassed by the present disclosure. For example, such groups can also be depicted as , , or .

[0396] In specific embodiments, a guanidinium cation is selected from the group consisting of:

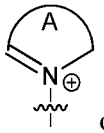
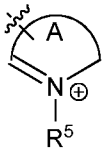


[0397] In certain embodiments, a polymerization - initiator comprises a carboxylate salt of a sulfonium group or an arsonium group:  or , wherein each of R^1, R^2, and R^3 are as defined above and described in classes and subclasses herein.

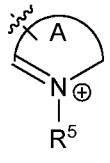
[0398] In specific embodiments, an arsonium cation is selected from the group consisting of:

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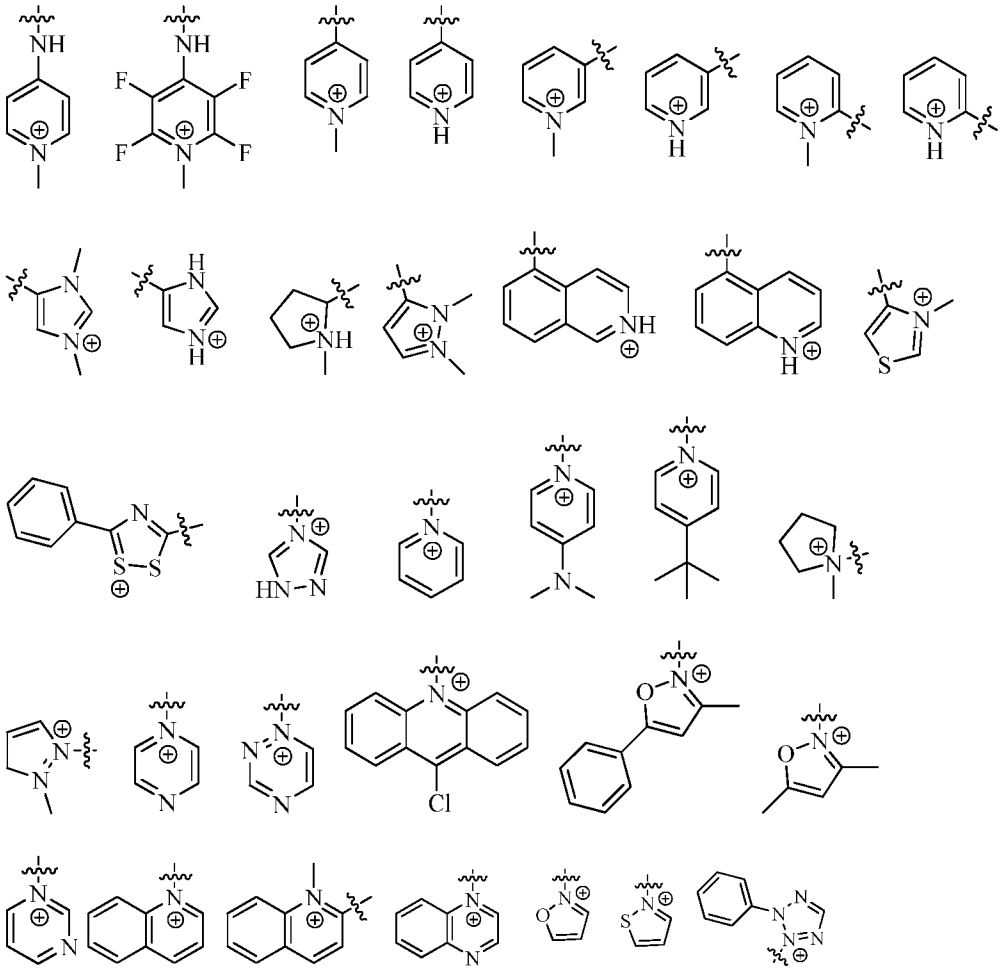
[0399] In certain embodiments, a polymerization initiator comprises a carboxylate salt of an optionally substituted nitrogen-containing heterocycle. In certain embodiments, the nitrogen-containing heterocycle is an aromatic heterocycle. In certain embodiments, the optionally substituted nitrogen-containing heterocycle is selected from the group consisting of: pyridine, imidazole, pyrrolidine, pyrazole, quinoline, thiazole, dithiazole, oxazole, triazole, pyrazolem, isoxazole, isothiazole, tetrazole, pyrazine, thiazine, and triazine.

[0400] In certain embodiments, a nitrogen-containing heterocycle includes a quaternarized nitrogen atom. In certain embodiments, a nitrogen-containing heterocycle includes an iminium moiety such as  or . In certain embodiments, the optionally substituted nitrogen-containing heterocycle is selected from the group consisting of pyridinium, imidazolium, pyrrolidinium, pyrazolium, quinolinium, thiazolium, dithiazolium, oxazolium, triazolium, isoxazolium, isothiazolium, tetrazolium, pyrazinium, thiazinium, and triazinium.

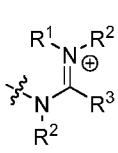
[0401] In certain embodiments, a nitrogen-containing heterocycle is linked to a metal complex via a ring nitrogen atom. In certain embodiments, a ring nitrogen to which the attachment is made is thereby quaternized, and In certain embodiments, linkage to a metal complex takes the place of an N-H bond and the nitrogen atom thereby remains neutral. In certain embodiments, an optionally substituted *N*-linked nitrogen-containing heterocycle is a pyridinium derivative. In certain embodiments, optionally substituted *N*-linked nitrogen-containing heterocycle is an imidazolium derivative. In certain embodiments, optionally substituted N-linked nitrogen-containing heterocycle is a thiazolium derivative. In certain embodiments, optionally substituted N-linked nitrogen-containing heterocycle is a pyridinium derivative.

[0402] In certain embodiments, a polymerization initiator comprises a carboxylate salt of . In certain embodiments, ring A is an optionally substituted, 5- to 10-membered heteroaryl group. In certain embodiments, Ring A is an optionally substituted, 6-membered heteroaryl group. In certain embodiments, Ring A is a ring of a fused heterocycle. In certain embodiments, Ring A is an optionally substituted pyridyl group.

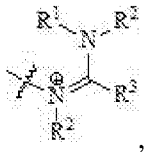
[0403] In specific embodiments, a nitrogen-containing heterocyclic cation is selected from the group consisting of:



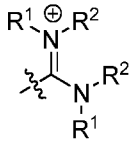
[0404] In certain embodiments, a polymerization initiator comprises a carboxylate salt of

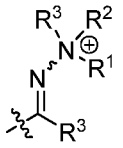


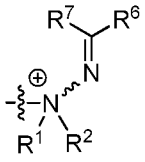
or



, where each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

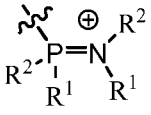
[0405] In certain embodiments, a polymerization initiator comprises a carboxylate salt of , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

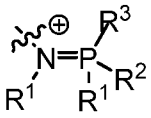
[0406] In certain embodiments, a polymerization initiator comprises a carboxylate salt of  wherein each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

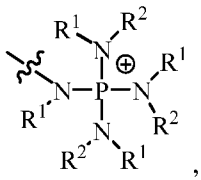
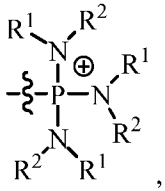
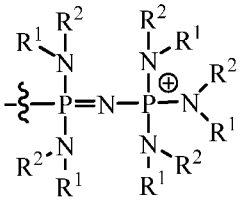
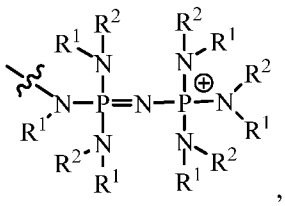
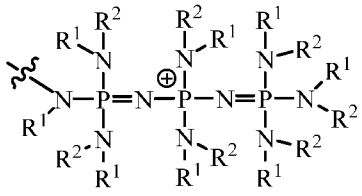
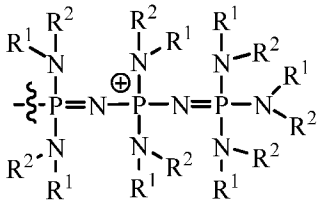
[0407] In certain embodiments, a polymerization initiator comprises a carboxylate salt of , wherein each of R^1, R^2, R^6, and R^7 is as defined above and described in classes and subclasses herein.

[0408] In certain embodiments, R^6 and R^7 are each independently an optionally substituted group selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl, and 8-10-membered aryl. In certain embodiments, R^6 and R^7 are each independently an optionally substituted C_{1-20} aliphatic. In certain embodiments, R^6 and R^7 are each independently an optionally substituted C_{1-20} heteroaliphatic having. In certain embodiments, R^6 and R^7 are each independently an optionally substituted phenyl or 8-10-membered aryl. In certain embodiments, R^6 and R^7 are each independently an optionally substituted 5- to10-membered heteroaryl. In certain embodiments, R^6 and R^7 can be taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3-C_{14} carbocycle, optionally substituted C_3-C_{14} heterocycle, optionally substituted C_6-C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl. In certain embodiments, R^6 and R^7 are

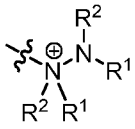
each independently an optionally substituted C_{1-6} aliphatic. In certain embodiments, each occurrence of R^6 and R^7 is independently methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or benzyl. In certain embodiments, each occurrence of R^6 and R^7 is independently perfluoro. In certain embodiments, each occurrence of R^6 and R^7 is independently $-CF_2CF_3$.

[0409] In certain embodiments, a polymerization initiator comprises a carboxylate salt of  wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

[0410] In certain embodiments, a polymerization initiator comprises a carboxylate salt of  wherein each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

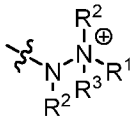
[0411] In certain embodiments, a cation is , , , , , or , wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

[0412] In certain embodiments, a polymerization initiator comprises a carboxylate salt of



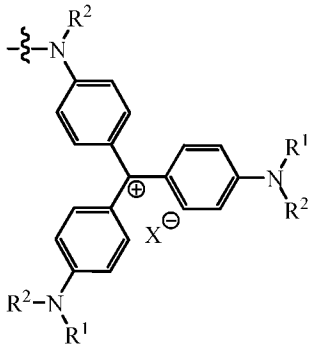
wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein.

[0413] In certain embodiments, a polymerization initiator comprises a carboxylate salt of



wherein each R^1, R^2, and R^3 is independently as defined above and described in classes and subclasses herein.

[0414] In certain embodiments, a polymerization initiator comprises a carboxylate salt of



, wherein each R^1 and R^2 is independently as defined above and described in classes and subclasses herein. In certain embodiments, suitable initiator include transition metal compounds. In certain embodiments, suitable catalysts include acid catalysts. In certain embodiments, the catalyst is a heterogeneous catalyst.

[0415] In some embodiments, the homogeneous polymerization initiator is a quaternary ammonium salt (for example, tetrabutylammonium (TBA) acrylate, TBA acetate, trimethylphenylammonium acrylate, or trimethylphenylammonium acetate) or a phosphine (for example, tetraphenyl phosphonium acrylate).

[0416] In some embodiments, the catalyst is tetrabutylammonium acrylate, sodium acrylate, potassium acrylate, iron chloride, tetrabutylammonium acetate,

trimethylphenylammonium acrylate, trimethylphenylammonium acetate, or tetraphenyl phosphonium acrylate.

[0417] With reference to FIG. **4A**, the polymerization catalyst in the first reactor (**408**) and the additional polymerization initiator in the second reactor (**410**) may be the same or different. For example, in some embodiments, wherein the same initiator is used in both reactors, concentration of initiator is not the same in each reactor.

[0418] In some embodiments, the homogeneous polymerization initiator is added to a polymerization reactor as a liquid. In other embodiments it is added as a solid, which then becomes homogeneous in the polymerization reaction. In some embodiments where the polymerization initiator is added as a liquid, the polymerization initiator may be added to the polymerization reactor as a melt or in any suitable solvent. For example, in some variations GAA, molten PPL or bPL is used as a solvent.

[0419] In some embodiments, the solvent for the polymerization initiator is selected such that the initiator is soluble, the solvent does not contaminate the product polymer, and the solvent is dry. In some variations, the polymerization initiator solvent is GAA, molten PPL, or bPL. In certain variations, solid PPL is added to a polymerization reactor, heated above room temperature until liquid, and used as the polymerization initiator solvent. In other embodiments, bPL is added to the polymerization reactor, cooled below room temperature until liquid, and used as the polymerization initiator solvent.

[0420] In some variations, the solid or liquid polymerization initiator (as a melt or as a solution in a suitable solvent) is prepared in one location, then shipped to a second location where it is used in the polymerization reactor. In other embodiments, the solid or liquid polymerization initiator (as a melt or as a solution in a suitable solvent) is prepared at the location of the polymerization reactor (for example, to reduce exposure to moisture and/or oxygen).

[0421] A solid or liquid polymerization initiator (as a melt or as a solution in a suitable solvent) may be pumped into a stirred holding tank or directly into the polymerization reactor.

[0422] In some variations, the liquid initiator and/or initiator precursors are dispensed from a shipping vessel/container into an intermediate, inert vessel to be mixed with suitable solvent, and then the initiator solution is fed to the reactor or a pre-mix tank. The initiator preparation system and the connections may be selected in such a way to ensure that the initiator or precursors are not contacted by ambient atmosphere.

[0423] In some variations, the polymerization reactor is a PFR, the solid or liquid initiator (as a melt or as a solution in a suitable solvent) and bPL are fed to a small stirred tank and then the mixture is fed to the PFR. In other embodiments, the bPL and the liquid catalyst are fed to a pre-mixer installed at the inlet of the PFR. In yet another embodiment, the PFR has a static mixer, the reaction occurs on the shell side of the reactor, and the solid or liquid initiator and bPL are introduced at the inlet of the reactor and the static mixer elements mix the initiator and bPL. In still another embodiments, the PFR has a static mixer, the reaction occurs on the shell side of the reactor, and the solid or liquid initiator is introduced into the PFR using metering pumps/feeders at multiple locations distributed along the lengths of the reactor.

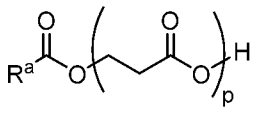
[0424] In some embodiments, the homogeneous polymerization initiator is delivered to the location of the polymerization reactor as a solid (for example, solid Al(TPP)Et, solid sodium acrylate, solid potassium acrylate, solid sodium acetate, solid potassium acetate, or solid TBA acrylate), the solid initiator is unpacked and loaded in hoppers under inert conditions (CO or inert gas), and the solids from hoppers can be fed directly inot the polymerization reactor, or be mixed with bPL prior to the reactor, or be metered into a suitable solvent before pumping into the polymerization reactors or mixing tanks.

Heterogeneous System

[0425] Any suitable polymerization catalyst may be used in the polymerization process to convert the production stream entering the polymerization process to the PPL product stream. In some embodiments, the polymerization catalyst is heterogeneous with the polymerization reaction mixture. Any suitable heterogeneous polymerization catalyst capable of polymerizing bPL in the production stream to produce the PPL product stream may be used in the methods described herein.

[0426] In some embodiments, the heterogeneous polymerization catalyst comprises any of the homogeneous polymerization catalysts described above, supported on a heterogeneous support. Suitable heterogeneous supports may include, for example, amorphous supports, layered supports, or microporous supports, or any combination thereof. Suitable amorphous supports may include, for example, metal oxides (such as aluminas or silicas) or carbon, or any combination thereof. Suitable layered supports may include, for example, clays. Suitable microporous supports may include, for example, zeolites (such as molecular sieves) or cross-linked functionalized polymers. Other suitable supports may include, for example, glass surfaces, silica surfaces, plastic surfaces, metal surfaces including zeolites, surfaces containing a metallic or chemical coating, membranes (comprising, for example, nylon, polysulfone, silica), micro-beads (comprising, for example, latex, polystyrene, or other polymer), and porous polymer matrices (comprising, for example, polyacrylamide, polysaccharide, polymethacrylate).

[0427] In some variations, the heterogeneous polymerization catalyst comprises the carboxylate salt of any of the homogeneous polymerization catalysts described above, wherein the carboxylate is heterogeneous. For example, in certain embodiments, the carboxylate of the polymerization catalyst is a compound of Formula (**D**):


(**D**),

where *p* is from 0 to 9 and R^a is a non-volatile moiety. The term "non-volatile moiety," as used herein, refers to a moiety or material to which a carboxylate can be attached, and that renders the carboxylate (e.g., when p = 0) non-volatile to pyrolysis conditions. In some embodiments, a non-volatile moiety is selected from the group consisting of glass surfaces, silica surfaces, plastic surfaces, metal surfaces including zeolites, surfaces containing a metallic or chemical coating, membranes (comprising, for example, nylon, polysulfone, silica), micro-beads (comprising, for example, latex, polystyrene, or other polymer), and porous polymer matrices (comprising, for example, polyacrylamide, polysaccharide, polymethacrylate). In some embodiments, the non-volatile moiety has a molecular weight above 100, 200, 500, or 1000 g/mol. In some embodiments, the non-volatile moiety is part of a fixed or packed bed system. In some embodiments, the non-volatile moiety is part of a fixed or packed bed system comprising pellets (e.g., zeolite). In certain embodiments, *p* is from 0 to 5. In certain embodiments, the carboxylate salt of the polymerization catalyst is an acrylate salt (i.e., of compound of Formula (**D**) where p = 0).

[0428] In some embodiments, the heterogeneous polymerization catalyst is a solid-supported quaternary ammonium salt (for example, tetrabutylammonium (TBA) acrylate, TBA acetate, trimethylphenylammonium acrylate, or trimethylphenylammonium acetate) or a phosphine (for example, tetraphenyl phosphonium acrylate).

[0429] In some embodiments, the catalyst is solid-supported tetrabutylammonium acrylate, iron chloride, TBA acetate, trimethylphenylammonium acrylate, trimethylphenylammonium acetate, or tetraphenyl phosphonium acrylate.

[0430] In certain embodiments, conversion of the production stream entering the polymerization process to the PPL product stream utilizes a solid carboxylate catalyst and the conversion is conducted at least partially in the gas phase. In certain embodiments, the solid carboxylate catalyst in the polymerization process comprises a solid acrylic acid catalyst. In

certain embodiments, the production stream enters the polymerization process as a liquid and contacted with a solid carboxylate catalyst to form the PPL product stream. In other embodiments, the production stream enters the polymerization process as a gas and contacted with a solid carboxylate catalyst to form the PPL product stream.

[0431] In some variations, the polymerization catalyst is a heterogeneous catalyst bed. Any suitable resin may be used for such a heterogeneous catalyst bed. In one embodiment, the polymerization catalyst is a heterogeneous catalyst bed packed in a tubular reactor. In some embodiments, the polymerization reactor system comprises a plurality of heterogeneous catalyst beds, wherein at least one catalyst bed is being used in the polymerization reactor, and at least one catalyst bed is not being used in the polymerization reactor at the same time. For example, the catalyst bed not actively being used may be being regenerated for later use, or may be stored as a back-up catalyst bed in case of catalyst failure of the actively used bed. In one embodiment, the polymerization reactor system comprises three heterogeneous catalyst beds, wherein one catalyst bed is being used in the polymerization reactor, one catalyst bed is being regenerated, and one catalyst bed is being stored as a back-up in case of catalyst failure.

[0432] In some variations, the heterogeneous polymerization catalyst is prepared in one location, then shipped to a second location where it is used in the polymerization reactor. In other embodiments, the heterogeneous polymerization catalyst is prepared at the location of the polymerization reactor (for example, to reduce exposure to moisture and/or oxygen).

Solvents

[0433] In some embodiments, the polymerization process does not include solvent. In other embodiments, the polymerization process does include one or more solvents. Suitable solvents can include, but are not limited to: hydrocarbons, ethers, esters, ketones, nitriles, amides, sulfones, halogenated hydrocarbons, and the like. In certain embodiments, the solvent is selected such that the PPL product stream is soluble in the reaction medium.

[0434] Without wishing to be bound by any particular theory, it is believed that solvents comprising Lewis bases of low to moderate polarity improve the performance of the polymerization reaction. Thus, in certain embodiments, a polymerization solvent comprises a Lewis base and is less polar than 1,3-dioxane (ε = dielectric constant at 20 °C = 13.6). In certain embodiments, a polymerization solvent comprises a Lewis base and is less polar than ortho-difluorobenzene (ε = 13). In certain embodiments, a polymerization solvent comprises a Lewis base and is less polar than metadifluorobenzene (ε = 5). In certain embodiments, a polymerization solvent comprises a Lewis base with substantially the same polarity as 1 ,4-dioxane (ε = 2.2). In some embodiments, a polymerization solvent is less polar than a carbonylation solvent as measured by dielectric constant. In some embodiments, a polymerization solvent has a dielectric constant at 20°C of less than about 13.6, less than about 13, or less than about 5.

[0435] For example, with reference to polymerization process depicted in FIGS. **4A** and **4B**, reactors **408** and/or **410** may be configured to receive solvent. For example, in one variation, polymerization process may further include a solvent source configured to feed solvent into reactors **408** and **410**. In another variation, the bPL from production stream **402** may be combined with solvent to form the production stream containing bPL fed into reactor **408**. In yet another variation, the polymerization catalyst from polymerization catalyst sources **404** and/or **406** may be combined with a solvent to form polymerization catalyst streams fed into the reactors.

Polymerization Reactors

[0436] The one or more polymerization reactors in the polymerization process may be any suitable polymerization reactors for the production of the PPL product stream from the production stream entering the polymerization process. For example, the polymerization reactor may be a CSTR, loop reactor, or plug flow reactor, or a combination thereof. In some

embodiments, the polymerization process comprises a single reactor, while in other embodiments, the polymerization process comprises a plurality of reactors. In some variations, the bPL is completely converted to PPL in a polymerization reactor. In other variations, the bPL is not completely converted to PPL in a polymerization reactor, and the PPL stream exiting the polymerization reactor comprises unreacted bPL. In certain variations, the PPL stream comprising unreacted bPL is directed to a bPL/PPL separator to remove the bPL from the PPL. The bPL may then be recycled back into the polymerization reactor, as described, for example, in FIGS. **7**, **9**, **11** and **13** above.

[0437] In certain variations, the polymerization process comprises two reactors in series, wherein the purified bPL stream enters the first reactor and undergoes incomplete polymerization to produce a first polymerization stream comprising PPL and unreacted bPL, the first polymerization stream exits the outlet of the first reactor and enters the inlet of the second reactor to undergo additional polymerization. In some variations, the additional polymerization completely converts the bPL to PPL, and the PPL product stream exits the outlet of the second polymerization reactor.

[0438] In other variations, the additional polymerization incompletely converts the bPL to PPL, and the PPL product stream exiting the outlet of the second polymerization reactor comprises PPL and unreacted bPL. In certain variations, the PPL product stream enters a BPL /PPL separator to remove unreacted bPL from the PPL product stream. In certain variations, the unreacted bPL is recycled back into the polymerization process. For example, in some variations, the unreacted bPL is recycled to the first polymerization reactor or the second polymerization reactor, or both the first and the second polymerization reactors.

[0439] In some embodiments, the polymerization process comprises a series of one or more continuous CSTR reactors followed by a BPL/PPL separator (such as a wiped film evaporator (WFE) or flash tank evaporator operating under vacuum). In other embodiments, the

polymerization process comprises a series of one or more loop reactors followed by a BPL/PPL separator (such as a WFE or flash tank evaporator operating under vacuum). In yet other embodiments, the polymerization process comprises a series of one or more in a series of one or more CSTR reactors followed by a polishing plug flow reactor (PFR) or by a BPL/PPL separator (Wiped Film Evaporator or flash tank evaporator operating under vacuum). In still other embodiments, the polymerization process comprises a series of one or more PFR optionally followed by a BPL/PPL separator (such as a WFE or flash tank evaporator operating under vacuum).

[0440] In some embodiments, the polymerization process comprises greater than two polymerization reactors. For example, in certain embodiments, the polymerization process comprises three or more polymerization reactors, four or more polymerization reactors, five or more polymerization reactors, six or more polymerization reactors, seven or more polymerization reactors, or eight or more polymerization reactors. In some variations, the reactors are arranged in series, while in other variations, the reactors are arranged in parallel. In certain variations, some of the reactors are arranged in series while others are arranged in parallel.

[0441] FIGS. **4A** and **4B** depict exemplary PPL production system/production processs comprising two polymerization reactors connected in series, and a PPL purification and BPL recycle system with a wiped film evaporator (WFE) for recycling of unreacted bPL back into the polymerization reactors. With reference to FIG. **4A**, the polymerization process includes bPL source **402** and polymerization catalyst source **404**, configured to feed bPL and catalyst, respectively, into reactor **408**. Reactor **408** includes a bPL inlet to receive bPL from the bPL source and a polymerization catalyst inlet to receive polymerization catalyst from the polymerization catalyst source. In some variations, the bPL inlet is configured to receive the bPL from the bPL source at a rate of 3100 kg/hr, and the first polymerization catalyst inlet is

configured to receive the polymerization catalyst from the polymerization catalyst source at a rate of 0.1 to 5 kg/hr.

[0442] With reference again to FIG. **4A**, reactor **408** further includes a mixture outlet to output a mixture comprising PPL, unreacted bPL, and residual carbonylation catalyst to reactor **410**. Reactor **410** is a second reactor positioned after reactor **408**, and is configured to receive the mixture from reactor **408** and additional polymerization catalyst from polymerization catalyst source **406**. In some variation, the mixture inlet of the second reactor is configured to receive the mixture from the first reactor at a rate of 4500 kg/hr, and the second polymerization catalyst inlet is configured to receive additional polymerization catalyst from the catalyst source at a rate of 0.1 to 4 kg/hr.

[0443] With reference again to FIG. **4A**, reactor **408** further includes a mixture outlet to output a mixture comprising PPL, unreacted bPL, and residual carbonylation catalyst to evaporator **412**. In some variations, the mixture outlet is configured to output such mixture at a rate of 4500 kg/hr.

[0444] With reference to FIG. **4B**, the depicted polymerization process includes bPL source **422** and polymerization catalyst source **424**, configured to feed bPL and catalyst, respectively, into reactor **428**. Reactor **428** includes a bPL inlet to receive bPL from the bPL source and a polymerization catalyst inlet to receive polymerization catalyst from the polymerization catalyst source. In some variations, the bPL inlet is configured to receive the bPL from the bPL source at a rate of 3100 kg/hr, and the first catalyst inlet is configured to receive the catalyst from the catalyst source at a rate of 0.1 to 5 kg/hr.

[0445] With reference again to FIG. **4B**, reactor **428** further includes a mixture outlet to output a mixture comprising PPL, unreacted bPL, and residual carbonylation catalyst to reactor **430**. Reactor **430** is a second reactor positioned after reactor **428**, and is configured to receive the mixture from reactor **428** and additional polymerization catalyst from polymerization

catalyst source **426**. In some variation, the mixture inlet of the second reactor is configured to receive the mixture from the first reactor at a rate of 4500 kg/hr, and the second polymerization catalyst inlet is configured to receive additional polymerization catalyst from the polymerization catalyst source at a rate of 0.1 to 4 kg/hr.

[0446] In some variations, the mixture output from reactor **410** (FIG. **4A**) and reactor **430** (FIG. **4B**) is made up of at least 95 %wt PPL.

[0447] Such mixture may be output from the second reactor to an evaporator. Evaporator **412** (FIG. **4A**) and **432** (FIG. **4B**) may be, for example, a wiped film evaporator, thin film evaporator, or falling film evaporator. The evaporator is configured to produce a PPL product stream.

[0448] In some variations, the evaporator is configured to produce a PPL product stream having a purity of at least 98%, at least 98.5%, or at least 99%. In other variations, the evaporator is configured to produce a PPL product stream having less 0.6 % wt of bPL. In some variations, the PPL stream has trace amounts of carbonylation catalyst. For example, the PPL product stream may have 0.1 mM of cobalt from the carbonylation catalyst. In some variations, the trace amounts of carbonylation catalyst are subsequently removed from the PPL product stream by IER before thermolysis, as described above in FIGS. **6**, **7**, **10** and **11**.

[0449] In some variations, the polymerization process further includes one or more heat exchangers. With reference to FIG. **4A**, bPL from bPL source **402** may be passed through heat exchanger **414** before such BPL stream is fed into reactor **408**.

[0450] It should generally be understood that the polymerization is an exothermic reaction. Thus, in other variations, reactors **408** and **410** (FIG. **4A**) may further include a connection to at least one heat exchanger. With reference to FIG. **4B**, reactors **428** and **430** (FIG. **4B**) may further include a connection to at least one heat exchanger.

[0451] The reactors of polymerization process may include any suitable reactors, including, for example, continuous reactors or semi-batch reactors. In one variation, with reference to FIG. **4A**, the reactors may be continuous-flow stirred-tank reactors. The reactors may also include the same or different stirring devices. For example, in one variation, reactor **408** may include a low velocity impeller, such as a flat blade. In other variation, reactor **410** may include a low shear mixer, such as a curved blade.

[0452] A skilled artisan would recognize that the choice for the mixing device in each of the reactors may depend on various factors, including the viscosity of the mixture in the reactor. For example, the mixture in the first reactor may have a viscosity less than 1000 cP. If the viscosity is less than1000 cP, then a low velocity impeller may be desired. In another example, the mixture in the second reactor may have a viscosity greater than 2000 cP. If the viscosity is greater than 2000 cP, then a low shear mixer may be desired.

[0453] In another variation, with reference to FIG. **4B**, the reactors may be loop reactors.

[0454] It should be understood that while FIGS. **4A** and **4B** depict the use of two reactors configured in series, other configurations are considered. For example, in other exemplary variations of the polymerization process, three reactors may be employed. In yet other variations where a plurality of reactors is used in the polymerization process, they may be arranged in series or in parallel.

[0455] FIG. **5** depicts yet another exemplary polymerization process, which includes a BPL polymerization reactor. Polymerization reactor **500** includes mixing zone **510** configured to mix the production stream entering the polymerization process and catalyst, and a plurality of cooling zones **520** positioned after the mixing zone. Polymerization reactor **500** has reaction length **502**, wherein up to 95% of the bPL in the entering production stream is polymerized in the presence of the catalyst to form PPL in the first 25% of the reaction length. In some variations of the system depicted in FIG. **5**, the bPL is completely converted to PPL. Such a

system may be used, for example, in the complete conversion of bPL to PPL as described above for FIGS. **6**, **8**, **10** and **12**.

[0456] In some variations of a polymerization reactor, the plurality of cooling zones includes at least two cooling zones. In one variation, the plurality of cooling zones includes two cooling zones or three cooling zones.

[0457] For example, polymerization reactor **500** as depicted in FIG. **5** has three cooling zones **522**, **524** and **526**. In one variation, the three cooling zones are connected serially in the first 25% of the reaction length. In another variation, cooling zone **522** is configured to receive a mixture of bPL and the catalyst from the mixing zone at a rate of 3100 kg/hr; cooling zone **524** is configured to receive a mixture of the bPL, the catalyst and PPL produced in cooling zone **522** at a rate of 3100 kg/hr; and cooling zone **526** is configured to receive a mixture of the bPL, the catalyst, the PPL produced in cooling zone **522**, and PPL produced in cooling zone **524** at a rate of 3100 kg/hr.

[0458] In certain embodiments, the first 25% of the reaction length is a shell and a tube heat exchanger. In one variation, the shell may be configured to circulate a heat transfer fluid to maintain a constant temperature in reaction length **502**. In another variation, the tube heat exchanger is configured to remove heat produced in the first reaction zone.

[0459] With reference again to FIG. **5**, polymerization reactor **500** further includes end conversion zone **528** connected to plurality of cooling zones **520**. In some variations, the end conversion zone is configured to receive a mixture of the bPL, the catalyst, and the PPL produced in plurality of cooling zones at a rate of 3100 kg/hr. In one variation, the end conversion zone has no cooling load.

[0460] In one variation, the polymerization reactor is a plug flow reactor or a shell-and-tube reactor.

[0461] The one or more polymerization reactors used in the methods described herein may be constructed of any suitable material compatible with the polymerization. For example, the polymerization reactor may be constructed from stainless steel or high nickel alloys, or a combination thereof.

[0462] In some embodiments, the polymerization process comprises a plurality of polymerization reactors, and the polymerization catalyst is introduced only into the first reactor in the series. In other embodiments, the polymerization catalyst is added separately to each of the reactors in the series. For example, referring again to FIG. **4A**, depicted is a polymerization process comprising two CSTR in series, wherein polymerization catalyst is introduced to the first CSTR, and polymerization catalyst is separately introduced to the second CSTR. In other embodiments, a single plug flow reactor (PFR) is used, and polymerization catalyst is introduced at the beginning of the reactor, while in other embodiments polymerization catalyst is introduced separately at a plurality of locations along the length of the PFR. In other embodiments, a plurality of PFR is used, and polymerization catalyst is introduced at the beginning of the first PRF. In other embodiments, polymerization catalyst is introduced at the beginning of each PFR used, while in still other embodiments polymerization catalyst is introduced separately at a plurality of locations along the length of each PFR.

[0463] The polymerization reactor may comprise any suitable mixing device to mix the polymerization reaction mixture. Suitable mixing devices may include, for example, axial mixers, radial mixers, helical blades, high-shear mixers, or static mixers. Suitable mixing devices may comprise single or multiple blades, and may be top, bottom, or side mounted. The polymerization reactor may comprise a single mixing device, or multiple mixing devices. In some embodiments, a plurality of polymerization reactors is used, and each polymerization reactor comprises the same type of mixing device. In other embodiments, each polymerization reactor comprises a different type of mixing device. In yet other embodiments, some

polymerization reactors comprise the same mixing device, while others comprise different mixing devices

Preferred embodiments of polymerization sub-systems

[0464] In the preferred embodiments, distillation sub-system consists of (1) one or more polymerization reactors and (2) PPL purification/BPL recycle system.

Preferred BPL polymerization reactor

[0465] Polymerization of bPL can be performed in one or more reactors operating in series or parallel and in preferred embodiments the distillate stream consisting of essentially pure bPL (purity greater than 99.9wt%) with trace amounts of low- and high-boiling impurities (non limiting impurities are THF and Succinic Anhydride) is fed bPL Polymerization reactor. The bPL feed stream can be fed at the temperature of the bPL purification column overhead (50-100°C) or can be cooled to 20-50°C before being fed to the polymerization reactor.

[0466] The preferred combination of conditions for the polymerization of bPL include temperatures in the range 80-150°C, preferrably 120-145°C at pressures below or above atmospheric in the presence of polymerization initiator. The preferred initiators are quaternary amine and alkali metal salts of acrylic acid. Non limiting examples of polymerization initiators are Sodium Acrylate, Potassium Acrylate, Tetrabutylammonium Acrylate. The molar ratio of polymerization initiator to bPL is from 1:20000 to 1:100, preferably from 1:15000 to 1:500, preferably from 1:10000 to 1:1000, and most preferably from 1:8000 to 1:1500.

[0467] In such preferred embodiments, solid polymerization initiator is mixed with fresh bPL stream before the reactor; a high shear mixer can be used to achieve good mixing of bPL with initiator. In another embodiment, solid polymerization initiator is mixed with recycled bPL stream before the reactor; a high shear mixer can be used to achieve good mixing of bPL with initiator. In another embodiment, polymerization reactor if fed directly into the

polymerization reactor; optionally, an educator can be used to effectively mix solid initiator with all or part of bPL feed at the inlet to the reactor.

[0468] During polymerization of bPL to form PPL Acrylic Acid that acts as chain transfer agent can be formed in-situ. In some embodiments small amounts of acrylic acid can be fed to polymerization reactor to control molecular weight of PPL. To avoid radical polymerization of acrylic acid, radical polymerization inhibitors such as phenothiazine (PTZ) can be fed to the polymerization reactor. The concentration of radical polymerization inhibitor in the reactor is maintained at 50-500 ppm (by weight); preferred inhibitor concentration is in the range from 150 to 250 ppm.

[0469] If the plurality of polymerization reactors are operating in series, bPL can be fed to the first reactor only or bPL feed can be split between reactors in series. If the plurality of polymerization reactors are operating in series, a polymerization initiator can be fed to the first reactor only or initiator can be fed to each of the reactors in series.

[0470] In one of the preferred embodiments, polymerization of bPL can be conducted in one or more Continuous Stirred Tank Reactors (CSTR) operating in series. The polymerization reaction is exothermic and heat of the reaction can be removed by means known in the art such as an internal heat exchanger or jacket, an external heat exchanger (reaction mixture is circulated through external heat exchanger and cooled stream is returned to the reactor), evaporative cooling (reactor is equipped with attached condenser: bPL is evaporated from the reactor, condensed in the condenser, and cooled bPL stream is returned to the reactor). The reactors can be operated at atmospheric pressure, below atmospheric pressure, above atmospheric pressure.

[0471] In another preferred embodiment, polymerization of bPL can be conducted in one or more Loop Reactors operating in series. The reactors can be operated at or above atmospheric pressure. The temperatures of the surfaces in contact with the reaction mixture

containing bPL and PPL are kept at temperatures that prevent precipitation of PPL (PPL melting point is at about 70-80°C)

[0472] In another preferred embodiment, polymerization of bPL is conducted in the reactor system consisting of one or more CSTR or Loop Reactors followed by one or more Plug Flow Reactors (PFR). The temperatures of the surfaces in contact with the reaction mixture containing bPL and PPL are kept at temperatures that prevent precipitation of PPL (PPL melting point is at about 70-80°C)

[0473] The concentration of PPL in the stream exiting the reaction system (bPL conversion) is greater than 40wt%, preferably greater than 60wt%, preferably greater than 75wt%. The conversion of bPL can be greater than 80%, greater than 90%, greater than 95%, or greater than 99%. The stream exiting bPL polymerization system is fed forward to PPL purification and bPL recycle system. In one embodiment, polymerization reactor product stream consists of about 80wt% PPL, about 20wt% bPL, and polymerization initiator incorporated into PPL molecules.

Preferred PPL purification /BPL recycle system

[0474] The polymerization reactor product consisting of PPL product and unreacted bPL is fed forward to PPL purification and bPL recycle system. In preferred embodiments bPL can be separated from PPL in one or more flash evaporators operating under vacuum, or one or more Wiped Film Evaporators (WFE) operating under vacuum, or a combination thereof. To avoid decomposition of bPL within this system, surface temperatures in contact with bPL are kept below 200°C, preferably below 180°C, most preferably below 160°C. Recovered bPL is fed back to the polymerization reactor. Purified PPL contains less than 0.5wt% bPL, preferably less than 0.25wt% bPL, preferably less than 0.1wt% bPL, and preferably concentration of bPL in PPL product is less than 100 ppm. Most preferably PPL is fed forward to thermolysis reaction system for production of Acrylic Acid or pelletized for storage or shipment.

BPL Conversion

[0475] In some variations, between 5% and 100%, between 10% and 100%, between 20% and 100%, between 30% and 100%, between 40% and 100%, between 50% and 100%, between 60% and 100%, between 70% and 100%, between 80% and 100%, between 90% and 100, or between 95% and 100% of the bPL is converted to PPL in the polymerization process.

[0476] In some variations, bPL is partially converted to PPL in the polymerization process. For example, in some variations, complete conversion of bPL to PPL is greater than or equal to 75%, and partial conversion of bPL to PPL is less than 75%. In other variations, complete conversion of bPL to PPL is greater than or equal to 80%, and partial conversion of bPL to PPL is less than 80%. In other variations, complete conversion of bPL to PPL is greater than or equal to 85%, and partial conversion of bPL to PPL is less than 85%. In yet other variations, complete conversion of bPL to PPL is greater than or equal to 90%, and partial conversion of bPL to PPL is less than 90%. In yet other variations, complete conversion of bPL to PPL is greater than or equal to 95%, and partial conversion of bPL to PPL is less than 95%. In one variation, complete conversion of bPL to PPL is greater than or equal to 99%, and partial conversion of bPL to PPL is less than 99%.

[0477] In other variations, partial conversion is between 30% and 90%; between 40% and 90%, between 50% and 90%; or between 60% and 90%.

[0478] In some variations, the polymerization process comprises a plurality of polymerization reactors, and the conversion of bPL to PPL in each reactor is between 5% and 100%, between 10% and 100%, between 20% and 100%, between 30% and 100%, between 40% and 100%, between 50% and 100%, between 60% and 100%, between 70% and 100%, between 80% and 100%, between 90% and 100, or between 95% and 100% of the bPL is converted to PPL.

[0479] In some variations, the polymerization process comprises a plurality of polymerization reactors, and the conversion of bPL to PPL over the entire polymerization process is between 5% and 100%, between 10% and 100%, between 20% and 100%, between 30% and 100%, between 40% and 100%, between 50% and 100%, between 60% and 100%, between 70% and 100%, between 80% and 100%, between 90% and 100, or between 95% and 100% of the bPL is converted to PPL.

[0480] In one variation, two reactors are operated in series, and the conversion of bPL to PPL in each reactor is between 10% and 100%.

[0481] As described above in FIGS. **9-13**, in some embodiments of the methods to produce PPL as described herein, the bPL is completely converted to PPL. In other embodiments, the bPL is partially converted to PPL.

BPL Conversion

[0482] Without wishing to be bound by any theory, the polymerization of bPL to PPL proceeds quickly when the concentration of reactants is high and the concentration of products is low. As the reaction progresses to produce more products, the driving force for conversion is reduced. This phenomenon leads reactors which perform full conversion to be larger than those that perform partial conversion. Thus, in certain embodiments, the polymerization conditions and reactor size are selected such that conversion of bPL to PPL is partial (for example, 70% conversion), and a bPL/PPL separation device (for example, a WFE or distillation column) is used to recycle reactants back to the inlet of the reactor. Without wishing to be bound by any theory, this may avoid the requirements of a relatively large reactor while still generating a relatively pure product. In addition, the unreacted bPL is removed, which may make the handling of PPL easier. In the case where no PPL is isolated, removal of bPL reduces the possibility of other products forming during the thermolysis reaction

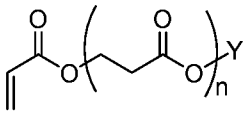
PPL Product Stream

[0483] In some embodiments, the production system/production process can produce at least about 2000 kg/hr PPL, at least about 2500 kg/hr PPL, at least about 3000 kg/hr PPL, at least about 3050 kg/hr PPL, or at least about 3500 kg/hr PPL, at least about 3638 kg/hr PPL, at least about 4000 kg/hr PPL, at least about 5000 kg/hr PPL, at least about 1000 kg/hr PPL, at least about 20000 kg/hr PPL, or at least about 35000 kg/hr PPL. In some embodiments, the production system/production process can produce about 2000 kg/hr PPL, about 2500 kg/hr PPL, about 3000 kg/hr PPL, about 3500 kg/hr PPL, about 3638 kg/hr PPL, about 4000 kg/hr PPL, about 5000 kg/hr PPL, about 1000 kg/hr PPL, about 20000 kg/hr PPL, or about 35000 kg/hr PPL. In some embodiments, the production system/production process can produce between 2000 kg/hr PPL and 3500 kg/hr PPL, between 2500 kg/hr PPL and 3500 kg/hr PPL, between bout 3000 kg/hr PPL and 3500 kg/hr PPL, between 2000 kg/hr PPL and 35000 kg/hr PPL, between 2500 kg/hr PPL and 35000 kg/hr PPL, between 3000 kg/hr PPL and 35000 kg/hr PPL, between 3500 kg/hr PPL and 35000 kg/hr PPL, between 3638 kg/hr PPL and 35000 kg/hr PPL, between 4000 kg/hr PPL and 35000 kg/hr PPL, between 5000 kg/hr PPL and 35000 kg/hr PPL, between 1000 kg/hr PPL and 35000 kg/hr PPL, or between 20000 kg/ PPL and 35000 kg/hr PPL.

[0484] In some embodiments, the production system/production process can produce at least about 25 kmol/hr PPL, at least about 30 kmol/hr PPL, at least about 40 kmol/hr PPL, at least about 42 kmol/hr PPL, or at least about 50 kmol/hr PPL. In some embodiments, the mass fraction of PPL in the PPL product stream in the production system/production process after polymerization can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.982, and at least about 0.99. In some embodiments, the mole fraction of PPL in the PPL product stream of the production system/production process after polymerization can be at least about 0.90, at least about at least about 0.95, at least about 0.98, at least about 0.984, and at least about 0.99. The remainder of the PPL product stream can include unreacted

bPL (in mole fraction of at most about 0.02, at most about 0.015, or at most about 0.011), secondary reaction products such as succinic anhydride (in mole fraction of at most about 0.01, at most about 0.005, or at most about 0.004,) and left over solvent (e.g., THF) and leftover carbonylation catalyst or components thereof (in at most about 1000 ppm). The PPL product stream can then receive thermolysis processing to form GAA. In some embodiments, the PPL product stream of the production system/production process can have a temperature between about 50-150°C, between about 110-150°C, or about 145°C. In some embodiments, the PPL product stream of the production system/production process can be at a pressure of at least about 0.001 bar, about 0.001-1 bar, or at least about 0.005 bar.

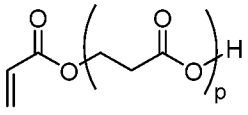
[0485] In certain embodiments, a method is provided for the production (e.g., integrated production) of a composition comprising PPL chains of Formula (**B**):



(**B**)

where *n* is an integer from 10 to about 1,000 and Y is either –H or a cation,

comprising the step of polymerizing bPL in the presence of a chain transfer agent selected from the group consisting of: a compound of Formula (**C**):



(**C**)

or a salt thereof, or a mixture of any two or more of these, where *p* is from 0 to 9. In certain embodiments, the composition further comprises PPL.

[0486] In certain embodiments, the PPL composition formed is characterized in that at least 90%, 95%, 99%, 99.5%, 99.8 or 99.9% of the polymer chains in the composition have an acrylate end group.

[0487] In certain embodiments, the PPL composition formed is characterized in that at least 90%, 95%, 99%, 99.5%, 99.8 or 99.9% of the polymer chains in the composition are of Formula (**B**).

[0488] In certain embodiments, *n* is, on average in the polypropiolactone composition, between 10 and 50, or between 50 and 100, or between 100 and 150, or between 150 and 250, or between 250 and 350, or between 350 and 500.

[0489] In some embodiments, the system described herein is configured to produce polypropiolactone with an average molecular weight between 800 g/mol and 100000 g/mol, between 500 g/mol and 70000 g/mol, between 1000 g/mol and 60000 g/mol, or between 1500 g/mol and 40000 g/mol. In some embodiments, the molecular weight is number average molecular weight, while in other embodiments, the molecular weight is weight average molecular weight.

[0490] In certain embodiments, the PPL composition is characterized in that it has a polydispersity index (PDI) of less than 10.

[0491] In certain embodiments, the PPL composition is characterized in that it has a PDI less than 8, or less than 5, or less than 3, or less than 2.5, or less than 2.0.

Cobalt/Ion Removal from PPL

[0492] In some embodiments, the PPL product stream is treated to reduce the concentration of cobalt and/or ions. The cobalt may be a cobalt ion or uncharged cobalt, or a combination thereof. The ions may be cobalt ions or non-cobalt ions.

[0493] In certain variations, the cobalt is a cobalt ion. The cobalt may be from decomposition of the carbonylation catalyst, residual catalyst components which comprise cobalt, or residual catalyst, or combinations thereof. For example, in some embodiments, the carbonylation catalyst decomposes to produce Co^{-1}, Co, Co^{+}, Co^{2+}, or Co^{3+}, or combinations

thereof. Thus, in some embodiments, the cobalt is a cobalt ion, while in other embodiments the cobalt is not a cobalt ion.

[0494] In some variations, at least some ions are removed from the PPL product stream. In some variations, the ions comprise metal ions. In other embodiments, the ions comprise non-metal ions. In yet other embodiments, the ions comprise both metal and non-metal ions. As discussed above, in certain variations, the ions comprise cobalt ions. The ions may be from decomposition of the carbonylation catalyst, residual catalyst components which comprise ions, residual catalyst, or ions produced as byproducts of the carbonylation reaction, or combinations thereof. For example in some embodiments, the carbonylation catalyst decomposes to produce Co^{-1}, Co^{+}, Co^{2+}, Co^{3+}, or Al^{3+}, or combinations thereof. In other embodiments, ions produced as byproducts of the carbonylation reaction include acetate ($CH_3C(O)O^-$) or acrylate ($CH_2=CHC(O)O^-$), or a combination thereof.

[0495] In certain embodiments, the step of treating the PPL product stream to remove at least a portion of cobalt and/or ions comprises ion exchange of cobalt and/or ions using ion exchange materials. In some embodiments, it may be possible to use an ion exchange resing for the ion exchange material. The ion exchange materials may be cationic, anionic, amphoteric, Lewis basic, Lewis acidic, or may comprise chelating groups. In certain embodiments, the ion exchange material may be a cation exchanger. In certain embodiments, functional groups on the cation exchange materials may be selected from: $–SO_3$, PO_3^{2-}, –COOH, $–C_6H_4OH$, –SH, $–AsO_3$, or $–SeO_3$, or combinations of two or more of these. In certain embodiments, functional groups on the cation exchange materials comprise $–SO_3$.

[0496] In certain embodiments, the ion exchange material may be an anion exchanger. In certain embodiments, functional groups on the anion exchange materials may be selected from: $–N^+(alkyl)_3$, $–N^+(CH_3)_3$, $–N^+(CH_3)_2C_2H_4OH$, $–N^+(CH_3)_2C_2H_5$, $–P^+(alkyl)_3$, $-P^+(aryl)_3$,–$P^+(C_4H_9)_3$, or $–P^+(Ph)_3$, or combinations of two or more of these. In certain embodiments,

functional groups on the anion exchange materials comprise $-N^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(alkyl)_3$. In certain embodiments, functional groups on the anion exchange materials comprise $-P^+(aryl)_3$.

[0497] In certain embodiments where the step of treating the PPL product stream to separate cobalt and/or ions comprises ion exchange, the process entails both anion exchange and cation exchange. In certain embodiments the anion and cation exchange are performed concomitantly. In certain embodiments, the anion and cation exchange are performed sequentially. In certain embodiments, the anion exchange is performed first followed by cation exchange. In certain embodiments, the cation exchange is performed first followed by anion exchange. In certain embodiments, an organic ion exchange resin may prove useful in the separation step comprises an organic ion exchange resin. The general characteristics and properties of such resins are the same as previously described.

[0498] In various aspects, the bead size may be widely distributed, or may be very narrow, so-called mono-disperse resins. In embodiments where catalyst is removed from the PPL product stream by ion exchange, the ion exchange material can be contacted with the PPL product stream by any conventional method. This includes, but is not limited to: flowing the PPL product stream through a fixed bed of a solid ion exchange material (i.e. in the form of beads, granules or other particles); flowing the PPL product stream through a fluidized bed of adsorbent, flowing the PPL product stream through fabrics, meshes, or filtration plates comprising the ion exchange material, or slurrying the PPL product stream with the ion exchange material (typically followed by filtration, centrifugation, sedimentation or the like to remove the ion exchange material from the PPL product stream). In embodiments where the PPL product stream is flowed through a packed column of ion exchange material, it may be desirable to provide a plurality of such columns in parallel with a provision to switch the flow from one to another periodically. Thus when one column of ion exchange material becomes

saturated with cobalt and/or ions removed from the PPL product stream, it can be switched out of the flow path and the flow diverted to a fresh column---in certain embodiments, the interval of time from when a column is placed in the flow path to when it is switched out of the flow path corresponds to the "first time interval" recited in the methods described herein.

[0499] Where an ion exchange material is used to remove cobalt and/or ions from the PPL product stream, the inventive methods may include a subsequent step of removing the cobalt and/or ions from the ion exchange material. Such removal methods are well known in the art and typically involve contacting the ion exchange resin with a strong solution of a salt, the anion or cation of which will displace the adsorbed component from the ion exchange material.

[0500] In certain variations, the cobalt is Co^{-1}, Co, Co^{+}, Co^{2+}, or Co^{3+}, or a combination thereof. In some embodiments, the PPL product stream prior to cobalt removal has a cobalt concentration between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, between 0.05 mM and 0.2 mM, or between 0.07 mM and 0.15 mM. In some embodiments, the cobalt concentration of the permeate prior to cobalt removal is about 0.01 mM, about 0.03 mM, about 0.06 mM, about 0.09 mM, about 0.1 mM, about 0.13 mM, about 0.16 mM, about 0.19 mM, about 0.2 mM, about 0.23 mM, about 0.26 mM, about 0.29 mM, or about 0.3 mM. In one embodiment, the cobalt concentration of the PPL before cobalt removal is about 0.1 mM.

[0501] Thus, in some embodiments, the concentration of cobalt in the PPL product stream before contacting the ion exchange resin is between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, between 0.05 mM and 0.2 mM, or between 0.07 mM and 0.15 mM.

[0502] In some embodiments, the concentration of cobalt in the PPL product stream after contacting the ion exchange resin is between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM

and 0.015 mM. In one variation, the concentration of cobalt in the PPL product stream after contacting the ion exchange resin is 0.01 mM.

[0503] In some embodiments, at least some aluminum is removed from the PPL product stream. In certain variations, the aluminum is Al^{3+}. In some embodiments, the PPL product stream prior to aluminum removal has an aluminum concentration between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, or between 0.09 mM and 0.2 mM. In some embodiments, the PPL product stream prior to aluminum removal has a aluminum concentration of about 0.01 mM, about 0.03 mM, about 0.06 mM, about 0.09 mM, about 0.1 mM, about 0.13 mM, about 0.16 mM, about 0.19 mM, about 0.2 mM, about 0.23 mM, about 0.26 mM, about 0.29 mM, or about 0.3 mM. In one embodiment, the aluminum concentration of the PPL product stream before aluminum removal is about 0.1 mM.

[0504] Thus, in some embodiments, the concentration of aluminum in the PPL product stream before contacting the ion exchange resin is between 0.001 mM and 5 mM, between 0.01 mM and 3 mM, between 0.01 mM and 2 mM, between 0.01 mM and 1 mM, between 0.05 mM and 0.5 mM, between 0.05 mM and 0.2 mM, or between 0.07 mM and 0.15 mM.

[0505] In some embodiments, the concentration of aluminum in the PPL product stream after contacting the ion exchange resin is between 0.001 mM and 1 mM, 0.001 mM and 0.5 mM, between 0.001 mM and 0.05 mM, between 0.005 mM and 0.02 mM, or between 0.007 mM and 0.015 mM. In one variation, the concentration of aluminum in the PPL product stream after contacting the ion exchange resin is 0.01 mM.

Solid PPL

[0506] In some embodiments, the production system/production process described herein further comprises a PPL stream processing system configured to receive the PPL product stream and produce solid PPL. For example, in one embodiment, the PPL product stream is

fed into at least one inlet of a PPL stream processing system, and solid PPL exits at least one outlet of the PPL stream processing system. The PPL stream processing system may be configured to produce solid PPL in any suitable form. For example, in some embodiments, the PPL stream processing system is configured to produce solid PPL in pelleted form, flaked form, granulated form, or extruded form, or any combinations thereof. Thus, solid PPL flakes, solid PPL pellets, solid PPL granules, or solid PPL extrudate, or any combinations thereof, may exit the outlet of the PPL stream processing system. The PPL stream processing system may include one or more flaking devices, pelleting devices, extrusion devices, or granulation devices, or any combinations thereof.

Geographic Location

[0507] In certain embodiments, the production system/production process described herein produces a PPL product stream at a first location, the PPL product stream is processed to produce solid PPL, and the solid PPL is converted to a GAA product stream in a second location. In some embodiments, the first location and the second location are at least 100 miles apart. In certain embodiments, the first location and the second location are between 100 and 12,000 miles apart. In certain embodiments, the first location and the second location are at least 250 miles, at least 500 miles, at least 1,000 miles, at least 2,000 or at least 3,000 miles apart. In certain embodiments, the first location and the second location are between about 250 and about 1,000 miles apart, between about 500 and about 2,000 miles apart, between about 2,000 and about 5,000 miles apart, or between about 5,000 and about 10,000 miles apart. In certain embodiments, the first location and the second location are in different countries. In certain embodiments, the first location and the second location are on different continents.

[0508] In certain embodiments, the solid PPL is transported from the first location to the second location. In some embodiments, the solid PPL is transported a distance of more than 100 miles, more than 500 miles, more than 1,000 miles, more than 2,000 miles or more than

5,000 miles. In certain embodiments, the solid PPL is transported a distance of between 100 and 12,000 miles, between about 250 and about 1000 miles, between about 500 and about 2,000 miles, between about 2,000 and about 5,000 miles, or between about 5,000 and about 10,000 miles. In some embodiments, the solid PPL is transported from a first country to a second country. In certain embodiments, the solid PPL is transported from a first continent to a second continent.

[0509] In certain embodiments, the solid PPL is transported from the North America to Europe. In certain embodiments, the solid PPL is transported from the North America to Asia. In certain embodiments, the solid PPL is transported from the US to Europe. In certain embodiments, the solid PPL is transported from the US to Asia. In certain embodiments, the solid PPL is transported from the Middle East to Asia. In certain embodiments, the solid PPL is transported from the Middle East to Europe. The solid PPL may be transported by any suitable means, including, for example, by truck, train, tanker, barge, or ship, or any combinations of these. In some embodiments, the solid PPL is transported by at least two methods selected from truck, train, tanker, barge, and ship. In other embodiments, the solid PPL is transported by at least three methods selected from truck, train, tanker, barge, and ship.

[0510] In some embodiments, the solid PPL is in the form of pellets, flakes, granules, or extrudate, or any combination thereof. In some variations, the solid PPL is converted to a GAA product stream using the thermolysis reactor as described herein. In some variations, the solid PPL is fed into an inlet of the thermolysis reactor and is converted to a GAA product stream. In other embodiments, the solid PPL is converted to molten PPL, and the molten PPL is fed into an inlet of the thermolysis reactor as described herein and converted to a GAA product stream.

Acrylic Acid Production system/production process

[0511] Polypropiolactone (PPL) can generally be converted to acrylic acid (AA) according to the following scheme:



PPL AA

[0512] In certain embodiments, the polypropiolactone produced undergoes thermolysis continuously (e.g. in a fed batch reactor or other continuous flow reactor format). In certain embodiments, the continuous thermolysis process is linked to a continuous polymerization process to provide acrylic acid at a rate matched to the consumption rate of the reactor.

Thermolysis Reactors

[0513] In some embodiments, the thermolysis reactor is a fluidized bed reactor. Inert gas may be used to fluidize inert solid heat transfer medium (HTM), and polypropiolactone is fed to the reactor. In some variations, the polypropiolactone may be fed to the reactor in molten form, for example, via a spay nozzle. The molten form may help facilitate the dispersion of polypropiolactone inside the reactor.

[0514] The reactor may be equipped with a cyclone that returns HTM solid back to the reactor. The inert gas, glacial acrylic acid, and higher boiling impurities (such as succinic anhydride and acrylic acid dimer) are fed from the cyclone to a partial condenser where impurities are separated. For example, the condenser may be used to condense the high boiling impurities, and such impurities can then be purged from the reactor as a residual waste stream.

[0515] Glacial acrylic acid with the inert gas may be fed to a second condenser where the glacial acrylic acid and the inert gas are separated. A liquid glacial acrylic acid stream is output from the second condenser, and the inert gas is output as a separate stream that may be returned

back to the reactor to fluidize the heat transfer solid. The glacial acrylic acid stream may be used for condensation/absorption and then storage.

[0516] The residual waste stream purged from the reactor may include, for example, high boiling organics (or organic heavies), for example, resulting from the polymerization catalyst and succinic anhydride, as well as the cationic and anionic carbonylation catalyst species if carbonylation catalyst was not separated prior to the thermolysis reactor. In some embodiments, the high boiling organics (or organic heavies) may include any compounds which are not acrylic acid. In certain embodiments, the high boiling organics (or organic heavies) may include any compounds which remain in the bottoms stream after condensing the acrylic acid in the glacial acrylic acid production system/production process. In some embodiments, the high boiling organics (or organic heavies) may include succinic anhydride, polymerization catalyst, or carbonylation catalyst or components thereof (for example, organic compounds from the carbonylation catalyst). In some embodiments, the high boiling organics (or organic heavies) have a boiling point higher than acrylic acid.

[0517] In other embodiments, the thermolysis reactor is a moving bed reactor. Polypropiolactone is fed into a moving bed reactor as a solid and glacial acrylic acid exits the reactor as a vapor stream and is then condensed.

Conditions

[0518] In some variations, the operating temperature in the thermolysis reactor is from about 150 °C to about 300 °C, from about 150 °C to about 200 °C, from about 150 °C to about 250 °C, from about 175 °C to about 300 °C, from about 200 °C to about 250 °C, from about 225 °C to about 275 °C, from about 250 °C to about 300 °C, from about 200 °C to about 300 °C, from about 200 °C to about 400 °C, or from about 200 °C to about 500 °C. In some variations, operating temperature is the average temperature of the contents of the reactor.

[0519] In some variations, the operating pressure in the thermolysis reactor is from about 0.01 atmospheres to about 500 atmospheres (absolute), from about 0.01 atmospheres to about 10 atmospheres (absolute), from about 0.01 atmospheres to about 50 atmospheres (absolute), from about 1 atmosphere to about 10 atmospheres (absolute), from about 1 atmosphere to about 50 atmospheres (absolute), from about 1 atmosphere to about 100 atmospheres (absolute), from about 10 atmospheres to about 50 atmospheres (absolute), from about 10 atmospheres to about 100 atmospheres (absolute), from about 50 atmospheres to about 100 atmospheres (absolute), from about 50 atmospheres to about 200 atmospheres (absolute), from about 100 atmospheres to about 200 atmospheres (absolute), from about 100 atmospheres to about 250 atmospheres (absolute), from about 200 atmospheres to about 300 atmospheres (absolute), from about 200 atmospheres to about 500 atmospheres (absolute), or from about 250 atmospheres to about 500 atmospheres (absolute).

[0520] In a particularly preferred embodiment the PPL stream from a bPL polymerization system enters primary thermolysis reactor, either in solid or liquid phase at a temperature between 100°C and 320°C, and absolute pressure between 1mmHg and 5000mmHg. One of many methods may provide heat transfer input, for example internal coils, external heat exchanger with a pump-around loop from and back to the primary reactor, or a baffled jacket on the walls of the reactor. Alternatively, a high temperature liquid or gas that that does not significantly affect the reaction chemistry may be introduced to maintain desired reaction temperature and separated downstream. Depending upon time and temperature residence time for complete conversion may vary from a few seconds to 24 hours or more. Mixing of the contents of the reactor may also improve mass and heat transfer.

[0521] Preferably the thermolysis conditions and arrangement will minimize the loss of PPL. to polyacrylic acid. Representative ways of avoiding polyacrylic acid production include the use of a depolymerization catalyst to decrease required reaction severity to decrease the

reaction rate of acrylic acid to polyacrylic acid relative to PPL to acrylic acid; the use of high concentrations of radical polymerization inhibitor; and/or means to minimize the concentration of acrylic acid in the liquid phase.

[0522] A continuous PPL thermolysis design (continuous, equal mass flows in and out of the primary reactor) can minimize the concentration of acrylic acid in the liquid phase, which lowers the reaction rate of acrylic acid to polyacrylic acid relative to that of PPL to acrylic acid. Removing vapors from the headspace of the primary reactor will lower the acrylic acid partial pressue in the headspace of the reactor and its liquid contents. Sparging with an inert gas, preferably continuously will further reduce the concentration of acrylic acid in the reactor's liquid contents. Withdrawal of liquid effluent stream and any other nonvolatile components may also be desired to manage accumulation of polyacrylic acid. These may be directed to a second thermolysis reactor, to waste treatment, or to a reactive distillation to convert the considerable PPL in the stream to volatile species such as acrylic acid and short-chain PPL oligomers. The vapor effluent from this distillation operation can flow back to the primary reactor, or be mixed with the vapor effluent from the primary reactor.

[0523] The vapor effluent from the various forms and number of suitable thermolysis reactor preferably, before going to product storage, undergoes condensation; passes in vapor phase to a distillation operation to remove higher-boiling and/or lower-boiling impurities before condensation; goes to condensation, then to a distillation in liquid phase to remove higher-boiling and/or lower-boiling impurities and then condensation. In another embodiment the the vapor effluent is condensed internally and isolated from the products that are non-volatile before undergoing further purification via distillation before storage or goes directly to product storage. Limiting the temperature of any liquid-phase acrylic acid is known to limit yields to polyacrylic acid. Preferably radical polymerization inhibitor shall be use in all liquid

phase acrylic acid. The bottoms from a distillation operation shall optimally be returned to the primary thermolysis reactor for further thermolysis, but may be disposed of as well.

[0524] In some variations, the thermolysis process is operated under an oxygen and water free atmosphere. For example, in certain variations, the amount of oxygen present in the thermolysis reactor is less than 1 wt%, less than 0.5 wt%, less than 0.01 wt%, or less than 0.001 wt %. In certain variations, the amount of water present in the thermolysis reactor is less than 1 wt%, less than 0.5 wt%, less than 0.01 wt%, or less than 0.001 wt%.

Glacial Acrylic Acid

[0525] In some variations, glacial acrylic acid produced according to the systems and methods described herein has a purity of at least 98%, at least 98.5%, at least 99%, at least 99.1%, at least 99.2%, at least 99.3%, at least 99.4%, at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%; or between 99% and 99.95%, between 99.5% and 99.95%, between 99.6% and 99.95%, between 99.7% and 99.95%, or between 99.8% and 99.95%.

[0526] In other variations, acrylic acid produced according to the systems and methods described herein is suitable to make high molecular weight polyacrylic acid. In certain variations, acrylic acid produced according to the systems and methods described herein may have a lower purity, such as 95%. Thus, in one variation, the acrylic acid has a purity of at least 95%.

[0527] In yet other variations, the glacial acrylic acid has:

(i) a cobalt level of less than 10 ppm, less than 100 ppm, less than 500 ppm, less than 1 ppb, less than 10 ppb, or less than 100 ppb; or

(ii) an aluminum level of less than 10 ppm, less than 100 ppm, less than 500 ppm, less than 1 ppb, less than 10 ppb, or less than 100 ppb; or

(iii) a β-propiolactone level of less than 1 ppm, less than 10 ppm, less than 100 ppm, less than 500 ppm, less than 1 ppb, or less than 10 ppb;

(iv) an acrylic acid dimer level of less than 2000 ppm, less than 2500 ppm, or less than 5000 ppm; or

(v) a water content of less than 10 ppm, less than 20 ppm, less than 50 ppm, or less than 100 ppm,

or any combination of (i) to (v).

[0528] Unlike known methods to produce glacial acrylic acid, acetic acid, furfurals and other furans are not produced and thus, are not present in the glacial acrylic acid produced.

[0529] Glacial acrylic acid may be used to make polyacrylic acid for superabsorbent polymers (SAPs) in disposable diapers, training pants, adult incontinence undergarments and sanitary napkins. The low levels of impurities present in the glacial acrylic acid produced according to the systems and methods herein help to facilitate a high-degree of polymerization to acrylic acid polymers (PAA) and avoid adverse effects from by-products in end applications. For example, aldehyde impurities in acrylic acid hinder polymerization and may discolor the polymerized acrylic acid. Maleic anhydride impurities form undesirable copolymers which may be detrimental to polymer properties. Carboxylic acids, e.g., saturated carboxylic acids that do not participate in the polymerization, can affect the final odor of PAA or SAP-containing products and/or detract from their use. For example, foul odors may emanate from SAP that contains acetic acid or propionic acid and skin irritation may result from SAP that contains formic acid. The reduction or removal of impurities from petroleum-based acrylic acid is costly, whether to produce petroleum-based crude acrylic acid or petroleum-based glacial acrylic acid. Such costly multistage distillations and/or extraction and/or crystallizations steps are generally employed (e.g., as described in U.S. Pat. Nos. 5,705,688 and 6,541,665).

GAA Production system/production process

[0530] In some embodiments, the production system/production process can produce at least about 25 kilo tons per annum ("KTA") glacial acrylic acid ("GAA"), at least about 160 KTA GAA, at least about 250 KTA GAA, or at least about 400 KTA GAA for annual production operation of about 8000 hours. In some embodiments, the production system/production process can produce at least about 2000 kg/hr GAA, at least about 2500 kg/hr GAA, at least about 3000 kg/hr GAA, at least about 3025 kg/hr GAA, at least about 3500 kg/hr GAA, at least about 3638 kg/hr GAA, at least about 4000 kg/hr GAA, at least about 5000 kg/hr GAA, at least about 1000 kg/hr GAA, at least about 20000 kg/hr GAA, or at least about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce about 2000 kg/hr GAA, about 2500 kg/hr PPL, about 3000 kg/hr GAA, about 3500 kg/hr GAA, about 3638 kg/hr GAA, about 4000 kg/hr GAA, about 5000 kg/hr GAA, about 1000 kg/hr GAA, about 20000 kg/hr GAA, or about 35000 kg/hr GAA. In some embodiments, the production system/production process can produce between 2000 kg/hr GAA and 3500 kg/hr GAA, between 2500 kg/hr GAA and 3500 kg/hr GAA, between bout 3000 kg/hr GAA and 3500 kg/hr GAA, between 2000 kg/hr GAA and 35000 kg/hr GAA, between 2500 kg/hr GAA and 35000 kg/hr GAA, between 3000 kg/hr GAA and 35000 kg/hr GAA, between 3500 kg/hr GAA and 35000 kg/hr GAA, between 3638 kg/hr GAA and 35000 kg/hr GAA, between 4000 kg/hr GAA and 35000 kg/hr GAA, between 5000 kg/hr GAA and 35000 kg/hr GAA, between 1000 kg/hr GAA and 35000 kg/hr GAA, or between 20000 kg/hr GAA and 35000 kg/hr GAA. In some embodiments, the production system/production process can produce at least about 25 kmol/hr GAA, at least about 30 kmol/hr GAA, at least about 35 kmol/hr GAA, at least about 40 kmol/hr GAA, at least about 42 kmol/hr, or at least about 50 kmol/hr GAA. The remainder of the GAA product stream can include secondary reaction products such as succinic anhydride and left over solvent such as THF. In some embodiments, the GAA product

stream of the production system/production process can have a temperature between about 20-60°C, between about 30-50°C, or about 40°C. In some embodiments, the GAA product stream of the production system/production process can be at a pressure of at least about 0.5 bar, about 0.5-1.5 bar, or at least about 1 bar.

Polymerization Examples

Example 1

Batch bPL polymerization using sodium acrylate as initiator

[0531] Under nitrogen, a Parr reactor equipped with an ATR-IR sentinel was charged with 16.2 mg of sodium acrylate. The reactor was sealed and heated to 100°C. In a 50 mL stainless vessel, a mixture of 11.8 mg of phenothiazine and 25 g of beta-propiolactone was added under nitrogen. The vessel was sealed and connected to the reactor. The mixture of beta-propiolactone and phenothiazine was injected into the reactor containing sodium acrylate with 50 psi of CO pressure at 100 °C. The reaction was agitated to 500 rpm, and monitored by in-line IR. The plot of beta-propionate peak at 1836 cm-1 and poly(propiolactone) peak at 1739 cm-1 as a function of time is shown in Figure 17. After the temperature was stabilized, the reaction temperature was set to 145 °C. And the reaction was run for 5 hours, by which time, the reaction went to completion.

[0532] The polymer formed in the reactor was extracted with CHCl3. Volatiles were stripped off by a rotovap. The polymer was further dried under a high vacuum to yield 21.8 g of a white solid. The solid was analyzed by 1H NMR, TGA, SEC, and melt rheology. SEC of the isolated solid gave am Mn of 3710 and an Mw of 8740.

Example 2

Batch bPL polymerization using tetra(butylammonium) acrylate as initiator

[0533] Under nitrogen, a Parr reactor equipped with an ATR-IR sentinel was charged with 12.2 mg of tetrabutylammonium acrylate. The reactor was sealed and heated to 100°C. In a

50 mL stainless vessel, 25 g of beta-propiolactone was added under nitrogen. The vessel was sealed and connected to the reactor. Into the reactor containing tetrabutylammonium acrylate, beta-propiolactone was injected with 50 psi of CO pressure at 100°C. The reaction was agitated to 500 rpm, and monitored by in-line IR. The plot of beta-propionate peak at 1836 cm^{-1} and poly(propiolactone) peak at 1739 cm^{-1} as a function of time is shown in Figure 21. After the temperature was stabilized, the reaction temperature was set to 140°C. At 36 min after the bPL addition, the reaction reached around 89% conversion, and 25 mL of water was added with 100 psi of CO at 140°C. After hydrolyzing the remaining beta-propiolactone, the polymer was extracted with CH_2Cl_2. Volatiles were removed using a rotovap and high vacuum to yield 17.7 g of a white solid. The solid was analyzed by ^1H NMR, TGA and melt rheology.

Example 2

Polymerization production using plug-flow reactor arrangement

[0534] A plug-flow reactor, consisting of two jacketed static mixers of ½" OD X 24 ¾" length and ~60 mL volume, an 3-way nitrogen/feed inlet ball-valve and an outlet with a jacketed viscometer (Cambridge Viscosity ViscoPro 2000 with 372 sensor), type K thermocouple, ATIR IR probe (Mettler-Toledo DS AgX CompTM and ReactIRTM 15) and a 0-250 psig back-pressure regulator, was heated to 140°C and purged with nitrogen at ambient pressure. A feed mixture was prepared by combining 0.1670 g of sodium acrylate (milled, sieved to 100 mesh and dried at 130°C under vacuum, 0.001776 mol), 0.1536 g phenothiazine and 670 mL of □-propiolactone (~ 760 g, 10.6 mol, chilled to -20°C) in a one liter, pressure/vacuum rated GL45 bottle equipped with a magnetic stir-bar in a glove-box. The bottle was closed with a three port GL45 cap equipped with a dip-tube and 2-way, 1/8" ball-valve on one port, a 1/8" 2-way-ball valve with a 1 psi cracking-pressure check-valve on the second port and a 1/8" 3-way ball-valve with one Luer-Lock fitting on the third port. The mixture was stirred briefly to dissolve the phenothiazine and suspend the sodium acrylate. The

sealed bottle was removed from the glove-box, transported to the plug-flow reactor, immersed in a water/ice bath on top of a magnetic stirrer and connected via the three 1/8" compression fittings to a feed pump, a vent line (to a scrubber filled with 2% sulfuric acid) and a nitrogen needle-valve, respectively. The mixture was stirred at 400 rpm to keep the sodium acrylate suspended. The 2-way vent-valve was opened followed by switching the 3-way nitrogen/fill valve from closed to nitrogen and adjusting the nitrogen needle-valve to give a steady stream of bubbles in the scrubber. The feed valve was then opened followed by a prime valve on the feed pump (Eldex Optos 2SM, 0.01 – 10.00 mL/min) and the pump was turned on at a flow rate of 5.00 mL/min and allowed to run until the (Teflon FEP) line from the prime port to the scrubber showed that all bubbles had been ejected. The pump was then turned off, flow set to 0.50 mL/min, prime/feed 3-way ball-valve switched to feed, the reactor inlet 3-way ball-valve switched from nitrogen to feed and the pump turned back on.

[0535] After 4 hours, the reactor exit back-pressure regulator was adjusted from ambient pressure to 200 psig and both the viscometer and the ReactIR were turned on. After another hour and a half, the reactor was fully pressurized, the viscometer (70 cP, compensated to 120°C) and ReactIR (~95% conversion) readings were steady and product was collected into a one liter collection bottle which contained 300 mL of magnetically stirred water. After a further 22.5 hours, the feed mixture was nearly exhausted and a 20 mL portion of chloroform was added to the feed bottle via syringe and the Luer-Lock fitting on the nitrogen/fill 3-way ball-valve. When the feed bottle was nearly empty again, another 20 mL of chloroform was added. When that charge had been consumed, a further 500 mL of chloroform was added. A fresh receiving bottle was placed on the reactor exit and conditions maintained for another 21 hours when feed pump and circulating bath were turned off.

[0536] The crude product mixture from the first receiver bottle was transferred to a large blender with an additional 500 mL of water, blended until no particles > 5 mm were observed

and the solid collected by filtration, air-dried and then vacuum dried at 40°C for 20 hours to give 562.1 grams of solid PPL product. The mixture of PPL solution in chloroform and aqueous liquid from the second receiver bottle was separated, the chloroform phase washed with water, dried and concentrated to 300 mL by azeotropic distillation and diluted in 600 mL of 2-propanol. The resulting precipitate was collected by filtration, air dried and then dried in vacuo at 40°C for 2 hours to give 90.5 grams of colorless solid PPL product. The filtrate was stripped of volatiles on a rotary evaporator at 50°C to give 45.0 g of clear, colorless oil, which separated into liquid and solid upon cooling.

[0537] 1H NMR analysis suggested that solid from the first receiver was composed of 556 grams of PPL, with a molecular weight of ~ 1210 g/mol with small amount (6 grams) of 3-hydroxypropionic acid (3-HPA) resulted from the hydrolysis of bPL in water (the GPC results showed Mn = 275, Mw = 1530 and Mn/Mw = 5.56). The isolated solid from the second receiver contained 90 grams of PPL with a molecular weight of 2030 g/mol (the GPC results showed Mn = 328, Mw = 1900, Mw/Mn = 5.79.) and 0.5 grams of 3-HPA.

Polymerization Examples

Example 4

Batch Thermolysis of PPL to Acrylic Acid

[0538] A lab-scale batch thermolysis system consisting of a two-necked round-bottom glass flask of 25mL approximate internal volume (the reaction flask) was carried out. The reaction flask was equipped with an internal thermocouple and the top center opening in the flask was equipped with a short-path distillation apparatus. The short-path distillation apparatus consisted of a short path still (similar to Ace Glass item #6554-06) with an additional thermocouple to monitor vapor temperature, followed by a water-cooled condenser, and finally a four-armed "cow" product receiver in a dry ice/acetone-cooled dewar. The reaction flask was set in a fabric heating mantle, the power to which was controlled by a temperature controller

that receives feedback from the thermocouple inside the reaction flask. Additional heat was provided with electric heat tape, wrapped around the top of the reaction flask and the distillation apparatus. The top of the reaction flask and the bottom of the distillation apparatus were insulated. The fabric heating mantle was set above a magnetic stir plate, and a PTFE-coated stir bar was added to the reaction flask.

[0539] The tared reaction flask was charged with 90mg dry sodium acrylate, 5mg PTZ, and 4.995g of PPL produced from ring-opening polymerization of solvent-free bPL in the presence of sodium acrylate (at a concentration of 1mol per 6,000mol of bPL) and phenothiazine (at a concentration of 200 ppmw in bPL). In addition, the tared product receiver was pre-charged with 5mg PTZ (distributed among the four product arms). After system assembly, the product receiver was attached to a nitrogen and vacuum source, and the air was displaced with nitrogen. Next, the reactor contents were heated to 90degC to melt and begin stirring. The system was brought under vacuum to an absolute pressure of approximately 700torr, and the reactor temperature setpoint was set to 210degC. Internal reflux was observed inside the reaction flask within minutes. It took 8-10minutes to heat reactor contents up to 210degC. The moment the reactor contents reached 210degC is defined as t=0. The reactor contents were held at 210degC for 10minutes, at which point the reactor flask was mostly empty, save for a glassy darker solid and the stir bar.

[0540] It was later determined that the residual material in the reaction flask weighed 156mg. Four product samples were obtained—sample 129-098A contained material collectred until t=2minutes, 129-098B contained material collected between t=2minutes and t=8minutes, 129-098C contained material between t=8minutes and t=9minutes, and 129-098D contained collected material between t=9minutes and t=10minutes, when heat sources were shut off. The total product collected weighed 4.7816g. Next, each sample was pipetted from the cow to labeled vials, and samples were taken for 1H NMR (see figures 25-28). NMR analysis suggests

an average acrylic acid content in 129-098A of 94.4%, in 129-098B of 90.7%, in 129-098C of 90.6%, and in 129-098D of 92.5% by mass. The balance consists of di-acrylic acid ester and traces of other PPL oligomers where n>2.

Polymerization Examples

Example 4

Batch Thermolysis of PPL to Acrylic Acid

[0541] A lab-scale batch thermolysis system consisting of a two-necked round-bottom glass flask of 50mL approximate internal volume (the reaction flask). The reaction flask was equipped with an internal thermocouple and the top center opening in the flask is equipped with a distillation apparatus. The distillation apparatus consisted of two Vigreux columns in series oriented coaxially (each similar to Ace Glass item #6578-04), followed by an adapter with an additional thermocouple to monitor vapor temperature, followed by a water-cooled condenser, and finally a 50mL round-bottom product receiver in a dry ice/acetone-cooled dewar. The reaction flask was set in a fabric heating mantle, the power to which is controlled by a temperature controller that receives feedback from the thermocouple inside the reaction flask. Additional heat was provided with electric heat tape, wrapped around the top of the reaction flask and the distillation apparatus. The top of the reaction flask and the bottom of the distillation apparatus are insulated. The fabric heating mantle was set above a magnetic stir plate, and a PTFE-coated stir bar is added to the reaction flask.

[0542] The tared reaction flask was charged with 1000mg dry sodium acrylate, 20mg PTZ, and 19.162g of PPL produced from ring-opening polymerization of solvent-free bPL in the presence of sodium acrylate (at a concentration of 1mol per 6,000mol of bPL) and phenothiazine (at a concentration of 200ppmw in bPL). In addition, the tared product receiver was pre-charged with 5mg PTZ. After system assembly, the product receiver was attached to a nitrogen and vacuum source, and the air was displaced with nitrogen. Next, the reactor

contents were heated to 90degC to melt and begin stirring. The system was brought under vacuum to an absolute pressure of approximately 90torr, and the reactor temperature setpoint was set to 165degC. Internal reflux was observed inside the reaction flask within minutes. It took approximately 10minutes to heat reactor contents up to 165degC. The moment the reactor contents reached 165degC is defined as t=0. The reactor contents were held at 165degC for 40minutes, at which point the reactor flask was still easily mixed by the stir bar.

[0543] It was later determined the residual material in the reaction flask weighed 4.7186g. Product sample 129-108 consisted of all collected product, and weighed 14.6586g. Next, a sample was taken for 1H NMR (see figure 29). NMR analysis suggests an average acrylic acid content in 129-108_Dist of 99.7%. The balance consists of di-acrylic acid ester and traces of other PPL oligomers where n>2.

[0544] This application discloses several numerical ranges in the text and figures. The numerical ranges disclosed inherently support any range or value within the disclosed numerical ranges even though a precise range limitation is not stated verbatim in the specification because this invention can be practiced throughout the disclosed numerical ranges.

[0545] The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, systems and methods described herein are not intended to be limited to the embodiments shown, but are to be accorded the widest scope consistent with the principles and features disclosed herein. Finally, the entire disclosure of the patents and publications referred in this application are hereby incorporated herein by reference.

CLAIMS

What is claimed is:

1. 1. A process for producing acrylic acid from a source of β-propiolactone, comprising:

contacting a BPL feed stream comprising β-propiolactone with a polymerization initiator in a polypropiolactone reaction zone having at least one polymerization reactor that produces a polypropiolactone outlet stream comprising polypropiolactone and β-propiolactone; and,

passing at least a portion of the polypropiolactone outlet stream to an acrylic acid production zone comprising a thermolysis reactor that receives the at least a portion of the polypriolactone outlet stream and produces an acrylic acid stream comprising acrylic acid.

2. The process of claim 1wherein the source of the β-propiolactone in the BPL feed stream isfrom ethylene oxide and carbon monoxide produced by:

contacting input components comprising carbon monoxide feed, an ethylene oxide feed, and a catalyst recylce stream with a carbonylation catalyst and a solvent in a carbonylation reaction zone and producing a BPL outlet stream comprising β-propiolactone, ethylene oxide and carbonylation catalyst;

passing at least a portion the BPL outlet stream to a carbonylation catalyst recycling zone and separating said portion into i) BPL separation stream comprising a portion of the BPL outlet stream from which at least some carbonylation catalyst has been removed and ii) the recycle stream, comprising β-propiolactone, solvent, ethylene oxide, carbonylation catalyst, succinic anhydride, and acetaldehyde;

passing at least a portion of the recycle stream to the carbonylation reaction zone;

purifying at least a portion of the BPL separation stream in a BPL purification zone comprising at least one separator, wherein the BPL purification zone produces a purified BPL stream and rejects a portion of β-propiolactone and rejects solvent, ethylene oxide, and carbonylation catalyst, succinic anhydride and acetaldehyde in one or more rejction streams streams comprising at least one of β-propiolactone, solvent, ethylene oxide, and carbonylation catalyst, succinic anhydride and acetaldehyde; and,

passing at least a portion of the purified BPL stream to the polypropiolactone reaction zone.

3. The process of claim 1 or 2 wherein the polymerization initiator is selected from the group consisting of quaternary ammonium salts, alkali metal salts of carboxylic acids, ammonium acrylate, ammonium acetate, phosphonium acrylate, phosphonium salts, sodium acrylate, potassium acrylate, phosphonium acetate, tetra-n-butylammonium acrylate, sodium acetate, potassium acetate, tetra-n-butylammonium acetate, trimethylphenylammonium acrylate, trimethylphenylammonium acetate, or tetraphenyl phosphonium acrylate and a radical polymerization inhibitor is present in the polypropiolactone reaction zone.

4. The process of any of claims 1-3 wherein the radical polymerization inhibitor comprises phenothiazine preferably in a concentration of 50-500 ppmw and more preferably in a concentration of 150 to 250 ppm.

5. The process of any of claims 1-4 wherein the polypropiolactone reactor zone comprises a first polymerization reactor and a second polymerization reactor; the first polymerization reactor produces an intermediate mixture comprising polypropiolactone, β-

propiolactone and polymerization initiator; the intermediate mixture and additional polymerization initiator passes to the second polymerization reactor that produces at least a portion of the polypropiolactone outlet stream; and at least a portion of the polypropiolactone outlet stream comprises polypropiolactone, β-propiolactone, and polymerization initiator.

6. The process of claim 5 wherein polypropiolactone is separated from the portion of the polypropiolactone outlet stream produced by the second reaction zone in at least one of an evaporator, flash tank evaporator, wiped film evaporator, or a distillation apparatus.

7. The process of any of claims 1 - 6 wherein the polypropiolactone outlet stream comprises a solid polypropiolactone.

8. The process of any of claim 1-7 wherein the at least one polymerization reaction zone contains at least one of a continuous reactor, semi-batch reactor, a continuous-flow stirred-tank reactor, a loop reactor, or plug-flow reactor and acrylic acid reaction zone comprises a thermolysis reactor for receiving molten propiolactone and the thermolysis reactor is in the form of a continuous stirred tank reactor, plug flow reactor, wiped film evaporator, a moving bed reactor, kneader reactor, and fluidized bed reactor.

9. The process of any of claims 1- 8 wherein at least a portion of the acrylic acid stream is separated into (i) an acrylic acid stream comprises acrylic acid having a purity of at least 90%, and (ii) an organic heavies stream.

10. The process of any of claims 2-8 wherein the BPL purification zone produces an EO rejection stream as one of the rejection streams, said EO rejection stream comprising ethylene oxide and at least a portion of the EO rejection is passed to the carbonylation reaction zone.

11. The process of claim and of claims 2-10 wherein the BPL purification zone produces a solvent recovery stream as one of the EO rejection streams, said solvent recovery stream comprising solvent at least a portion of the solvent recovery stream is passed to the carbonylation reaction zone.

12. The process of nay of claims 2-11 wherein I) the carbonylation catalyst recycling zone comprises one or more membrane systems from which the catalyst recycle stream is recovered as a retentate and BPL separation stream is recovered as a permeate; and II) the BPL purification zone comprises a.) an EO recovery section comprising at least one distillation column that receives at least a portion of the BPL separation stream and produces an EO stream containing ethylene oxide that is passed to the carbonylation reactor and a solvent bottoms stream containing solvent and β-propiolactone, b.) a solvent recovery section comprising at least one distillation column that receives at least a portion of the solvent bottoms stream and produces a overhead recovered solvent stream comprising solvent that is passed to the carbonylation zone and a BPL bottoms stream comprising β-propiolactone, and c.) a BPL concentration section comprising at least one distillation column that receives the BPL bottoms stream and produces an bottoms rejection stream and produces the the purified BPL as an overhead stream.

13. The process of any of claims 2-12 wherein the carbonylation catalyst is at least one of a cobalt-aluminum catalyst; a carbonyl cobaltate in combination with an aluminum porphyrin compound, a carbonyl cobaltate in combination with an aluminum salen compound, a carbonyl cobaltate in combination with an aluminum salophen compound, and Al(TPP)Co(CO)4).

14. The process of any of claim 2-13 wherein the carbonylation catalyst is at least partially dissolved in a catalyst solvent and the solvent comprises at least one an ether, a

hydrocarbon, tetrahydrofuran, hexane, 2,5-dimethyl tetrahydrofuran, sulfolane, N-methyl pyrrolidone, 1,3 dimethyl-2-imidazolidinone, diglyme, triglyme, tetraglyme, diethylene glycol dibutyl ether, isosorbide ethers, methyl tertbutyl ether, diethylether, diphenyl ether, 1,4-dioxane, ethylene carbonate, propylene carbonate, butylene carbonate, dibasic esters, diethyl ether, acetonitrile, ethyl acetate, propyl acetate, butyl acetate, 2-butanone, cyclohexanone, toluene, difluorobenzene, dimethoxy ethane, acetone, and methylethyl ketone.

15. The process of any of claims 2-14 wherein the carbonylation reaction zone: includes reactor operating conditions of temperatures of from -20°C to 160°C and pressures of from 100 psig to 5000 psig; at least one reactor selected from the group consisting of a continuous reactor or a semi-batch reactor a continuous-flow stirred-tank reactor or a loop reactor; and produces β-propiolactone with a selectivity of at least 90% and preferably at least 99%

16. The process of claim 2-15 wherein the BPL outlet stream satisfies on a mass fraction basis the condition of having; at least 0.1 and at most 0.4 β-propiolactone; at least 0. and at most 0.9 solvent; at least 0.005 and at most 0.07 ethylene oxide; between 0.0005 to 0.001 of carbon monoxide; at least 0.0001 and at most 0.005 catalyst; at least 0.0001 and at most 0.06 acetaldehyde; or at least 0.0001 and at most 0.06 succinic anhydride.

17. The process of any of claims 2-16 wherein the BPL concentration section includes a vacuum column and the purified BPL stream is recovered as a vacuum column overhead stream having a β-propiolactone purity of at least 99% and preferabaly at least 99.5% and most preferably 99.9%.

19. A process for producing acrylic acid from ethylene oxide and carbon monoxide, comprising:

contacting carbon monoxide feed, an ethylene oxide feed, an CO overhead stream and a BPL recycle stream with a carbonylation catalyst and a solvent in a carbonylation reaction zone and producing a BPL outlet stream comprising β-propiolactone, solvent, ethylene oxide, carbon monoxide, carbonylation catalyst, acetaldehyde, and succinic anhydride;

passing at least a portion of the BPL outlet stream to a CO/EO separator and recovering i.) the CO separator overhead stream wherein the CO separator overhead stream comprises ethylene oxide and carbon monoxide and ii.) an CO separator bottoms stream comprising β-propiolactone, solvent, carbonylation catalyst, acetaldehyde, succinic anhydride, and ethylene oxide;

passing at least a portion of the CO separator overhead stream to the carbonylation reaction zone;

passing at least a portion the CO separator bottoms stream to a membrane separation section of a carbonylation catalyst recycling zone and separating said at least a portion of the CO separator bottoms stream into i) a BPL recycle stream comprising a retentate containing separated carbonylation catalyst, solvent, and β-propiolactone and ii) a BPL separation stream comprising a permeate containing β-propiolactone, solvent, acetaldehyde, succinic anhydride, ethylene oxide and carbonylation catalyst;

passing at least a portion of the BPL recycle stream to the carbonylation reaction zone;

passing at least a portion of the BPL separation stream to a BPL purification zone comprising at least one separation zone that separates the BPL separation stream

into a solvent recycle stream comprising solvent, and a purified BPL stream comprising β-propiolactone and carbonylation catalyst;

passing at least a portion of the purified BPL stream and a polymerization initiator to a polypropiolactone reaction zone having at least one polymerization reactor that contacts the at least a portion of the purified BPL stream with the polymerization initiator and produces a polypropiolactone outlet stream comprising polypropiolactone and β-propiolactone;

passing at least a portion of the polypropiolactone outlet stream to a PPL/BPL processing zone having at least one separation zone to produce i.) an PPL/BPL overhead stream that increases the concentration of β-propiolactone relative to the polypropiolactone outlet stream and ii) a PPL/BPL separator bottoms stream that comprises polypropiolactone;

passing at least a portion of the PPL/BPL overhead stream to the polyproprionate reaction zone;

passing at least a portion of the a PPL/BPL bottoms stream to an acrylic acid production zone comprising a thermolysis reactor that receives the at least a portion of the a polypropiolactone outlet stream and produces an acrylic acid stream; and,

separating at least a portion of the acrylic acid stream in a separator into (i) acrylic acid stream comprising acrylic acid having a purity of at least 90%, and (ii) an organic heavies stream.

18. The process of claim 17 wherein the acrylic acid stream has a acrylic acid purity of greater than 99.5% and comprises glacial acrylic acid.

19. The process of any of claims 17-18 wherein the at least one polymerization reactor produces polypropiolactone at a polypropiolactone conversion of at least 50%.

20. The process of of any of claims 17-19 wherein the at least one separation zone in the PPL/BPL processing zone comprises at least one flash tank and/or at least one evaporator comprising a wiped film evaporator, thin film evaporator, or falling film evaporator; and the the CO separator is a flash tank.

21. The process of any of claims 17-20 wherein the carbonylation reactor zone operates at a temperature between 30°C and 160°C and a pressure between 100 psig and 5000 psig the at least one distillation column operates at or below atmospheric pressure and at a temperature of less than 120°C.

22. The process of of any of claims 17-21 wherein the solvent recycle stream comprises solvent and less than 15 wt% of β-propiolactone, ethylene oxide, carbon monoxide, acetaldehyde, or succinic anhydride, or any combinations thereof and wherein the purified BPL stream comprises (i) β-propiolactone and (ii) less than 1 wt% of solvent, ethylene oxide, carbon monoxide, acetaldehyde, or succinic anhydride, or any combinations thereof.

23. A process for producing acrylic acid from ethylene oxide and carbon monoxide, comprising:

contacting carbon monoxide feed, an ethylene oxide feed, an CO overhead stream and a BPL recycle stream with a carbonylation catalyst and a solvent in a carbonylation reaction zone and producing a BPL outlet stream comprising β-propiolactone, solvent, ethylene oxide, carbon monoxide, carbonylation catalyst, acetaldehyde, and succinic anhydride;

passing at least a portion of the BPL outlet stream to a CO separator and recovering i.) the CO overhead stream wherein the CO overhead stream comprises ethylene oxide and carbon monoxide and ii.) a CO bottoms stream comprising β-propiolactone, solvent, carbonylation catalyst, acetaldehyde, succinic anhydride, ethylene oxide and carbon monoxide;

passing at least a portion of the CO overhead stream to the carbonylation reaction zone;

passing at least a portion the CO bottoms stream to a membrane separation section of a carbonylation catalyst recycling zone and separating said at least a portion of the CO bottoms stream into i) a BPL recycle stream comprising a retentate containing separated carbonylation catalyst, solvent and β-propiolactone and ii) a BPL separation stream comprising a permeate containing β-propiolactone, solvent, acetaldehyde, succinic anhydride, ethylene oxide, carbon monoxide, and carbonylation catalyst;

passing at least a portion of the BPL recycle stream to the carbonylation reaction zone;

purifying the BPL separation stream in a BPL purification zone comprising at least one distillation column that further separates the BPL separation stream into a solvent recycle stream comprising solvent and a purified BPL stream comprising β-propiolactone;

passing at least a portion of the purified BPL stream and a polymerization initiator to a polypropiolactone reaction zone having at least one polymerization reactor that contacts the at least a portion of the purified BPL stream with the polymerization

initiator and produces a polypropiolactone outlet stream comprising polypropiolactone and β-propiolactone; and,

passing at least a portion of the polypropiolactone outlet stream to an acrylic acid production zone comprising a thermolysis reactor that receives the at least a portion of the polypropiolactone outlet stream and produces an acrylic acid stream; and,

separating at least a portion of the acrylic acid stream in a condenser into (i) an acrylic acid stream comprises acrylic acid having a purity of at least 90%, and (ii) an organic heavies stream.

24. The process of claim 23 wherein the acrylic acid stream has an acrylic acid purity of greater than 99.5% and comprises glacial acrylic acid.

25. The process of any of claims 23-24 wherein the at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone first passes to a polypropiolactone purification zone, comprising a PPL ion exchange zone comprising a resin column that purifies the at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone so that it comprises at least 90 wt% of polypropiolactone and removes an ionic species stream comprising cationic carbonylation catalyst species and anionic carbonylation catalyst species; and wherein at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone passes from the polypropiolactone purification zone first passes to a polypropiolactone processing zone before passing to the acrylic acid production zone and the polypropiolactone processing zone converts the at least a portion of the purified polypropiolactone outlet stream that passes to the acrylic acid production zone to solid form.

26. The process of any of claims 23-25 wherein a.) at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone passes from the polypropiolactone purification zone to a PPL/BPL processing zone before passing to the acrylic acid production zone and the PPL/BPL processing zone has at least one separation zone to produce i.) an overhead stream that increases the concentration of β-propiolactone in the at least a portion of the polypropiolactone outlet stream that passes to the acrylic acid production zone and ii.) a PPL/BPL bottoms stream that comprises polypropiolactone and b.) a condensate ion exchange zone comprising a resin column receives at least a portion of the organic heavies and separates the organic heavies into an heavies output stream and an ionic species stream comprising cationic carbonylation catalyst species and anionic carbonylation catalyst species.

27. A method for continuously producing polypropiolactone, comprising:

continuously feeding β-propiolactone into a first reactor;

continuously feeding polymerization initiator into the first reactor;

producing a first mixture comprising polypropiolactone and unreacted β-propiolactone in the first reactor,

wherein the first reactor comprises:

a β-propiolactone inlet to receive the β-propiolactone from a β-propiolactone source,

a first initiator inlet to receive the initiator from a initiator source, and

a first mixture outlet to output the first mixture; and

transferring the first mixture from the first reactor to a second reactor;

optionally feeding additional initiator from the initiator source to the second reactor;

producing a second mixture comprising polypropiolactone and unreacted β-propiolactone,

wherein the second reactor comprises:

a mixture inlet to receive the first mixture from the first reactor,

optionally, a second initiator inlet to receive the additional initiator from the initiator source, and

a second mixture outlet to output the second mixture.

28. A solid transportable polymer composition, comprising:

at least 95 wt% of polypropiolactone;

less than 1 ppm of cobalt or ions thereof;

less than 10 ppm of aluminum or ions thereof;

less than 10 ppm acetic acid;

less than 500 ppm of tetrahyrofuran; and

less than 10 ppm of succinic anhydride

less than 10 ppm β-propiolactone

less than 6000 ppm water

29. A β-propiolactone composition, comprising:

at least 99 wt% of β-propiolactone;

less than 10 ppm of cobalt or ions thereof;

less than 10 ppm of aluminum or ions thereof;

less than 300 ppm of acetic acid;

less than 500 ppm of succinic anhydride;

less than 500 ppm of tetrahyrofuran;

less than 100 ppm Ethylene Oxide;

less than 100 ppm acetaldehyde; an average molecular weight of polypropiolactone of between 800 and 100000 g/mol.

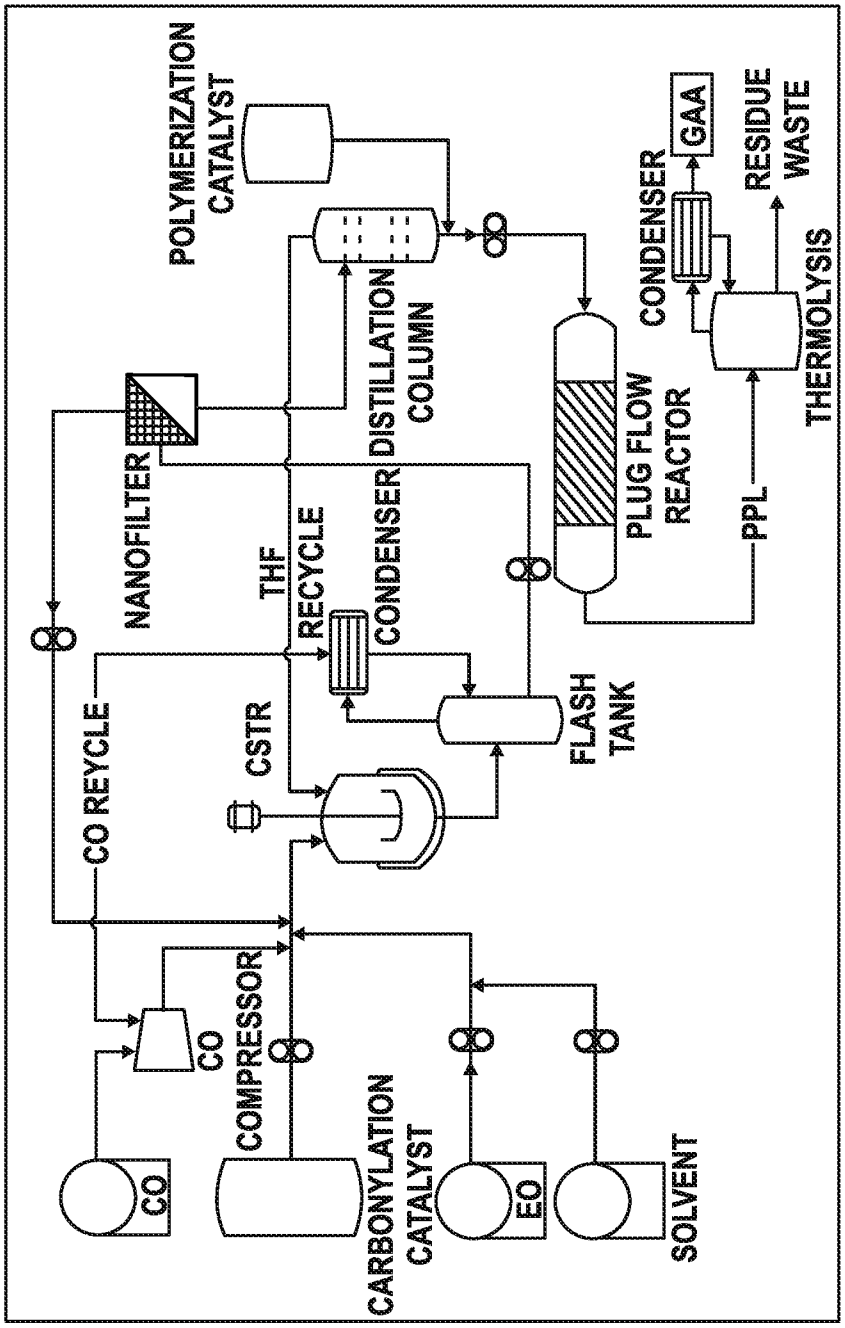

POLYMERIZATION CATALYST
DISTILLATION COLUMN
NANOFILTER
THF RECYCLE
CONDENSER
CSTR
CO REYCLE
FLASH TANK
PLUG FLOW REACTOR
PPL
CONDENSER
GAA
RESIDUE WASTE
THERMOLYSIS
CO
COMPRESSOR
CO
CARBONYLATION CATALYST
EO
SOLVENT

FIG. 1

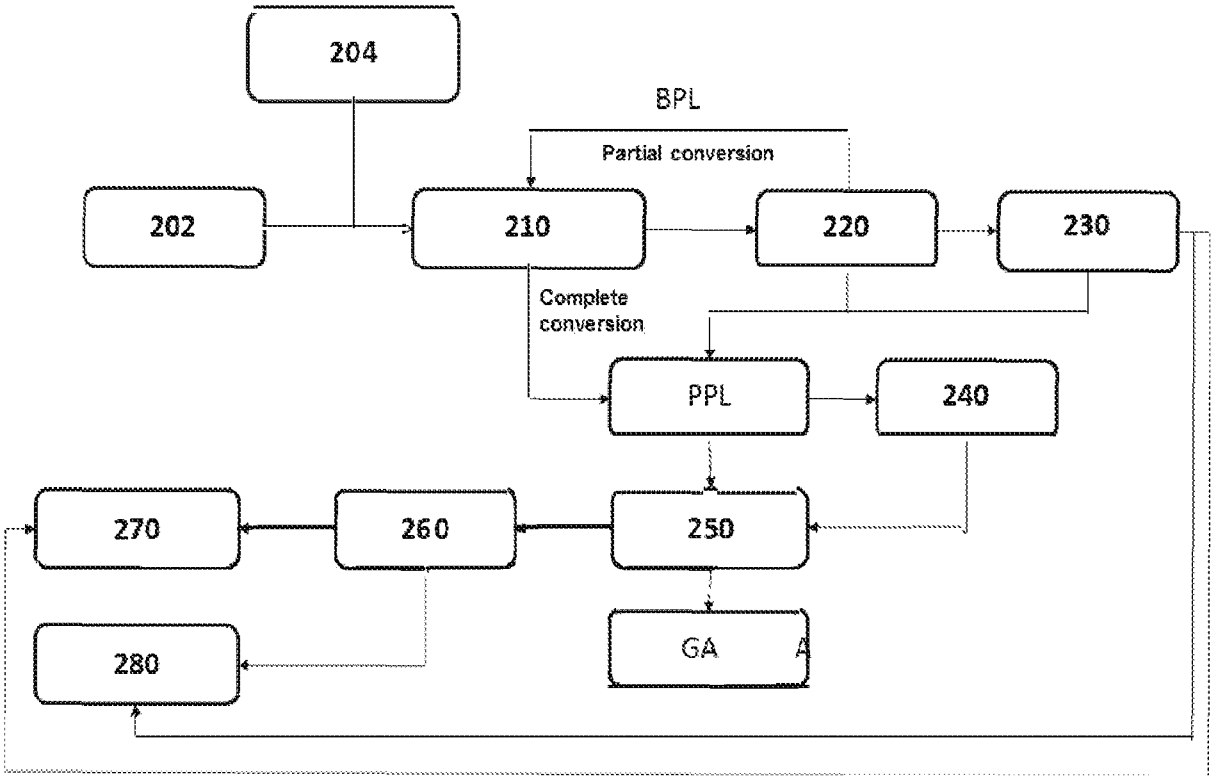

204
BPL
Partial conversion
202
210
220
230
Complete conversion
PPL
240
270
260
250
280
GA

FIG. 2

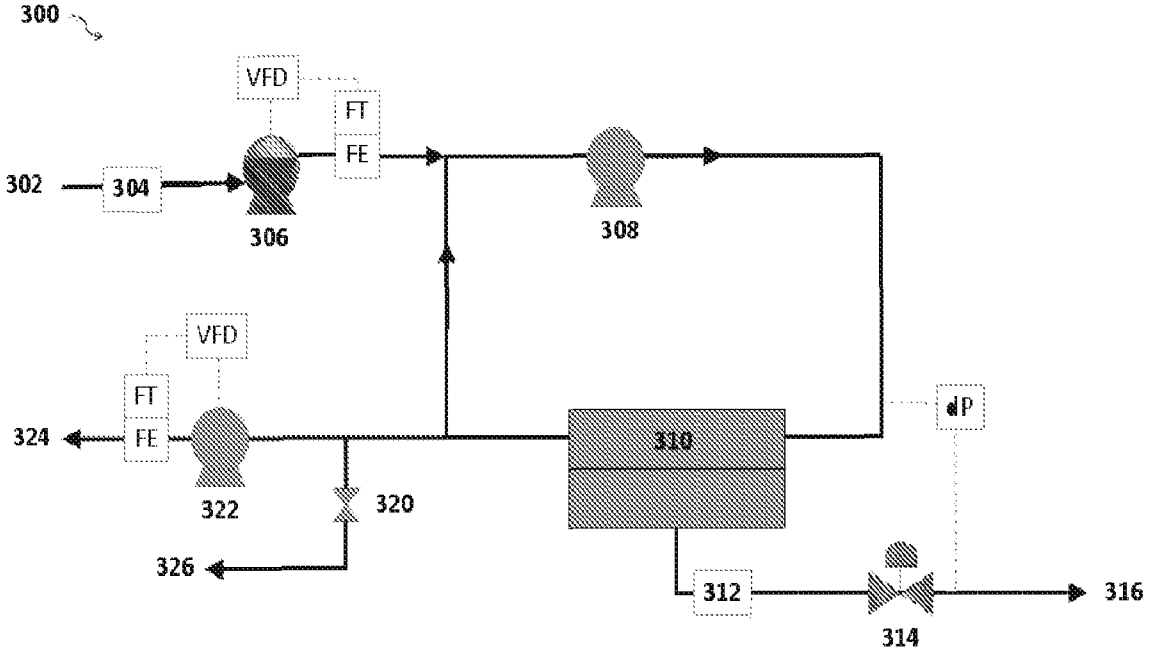

300
VFD
FT
FE
302
304
306
308
VFD
FT
FE
324
322
320
326
310
dP
312
314
316

FIG. 3

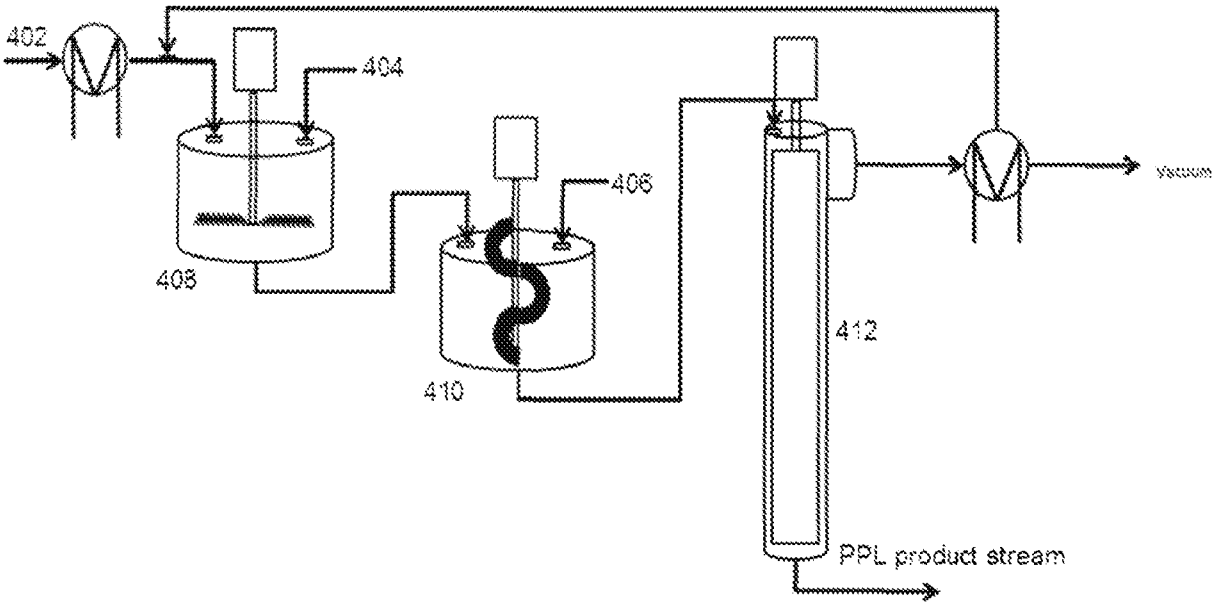

402
404
406
408
410
412
PPL product stream

FIG. 4A

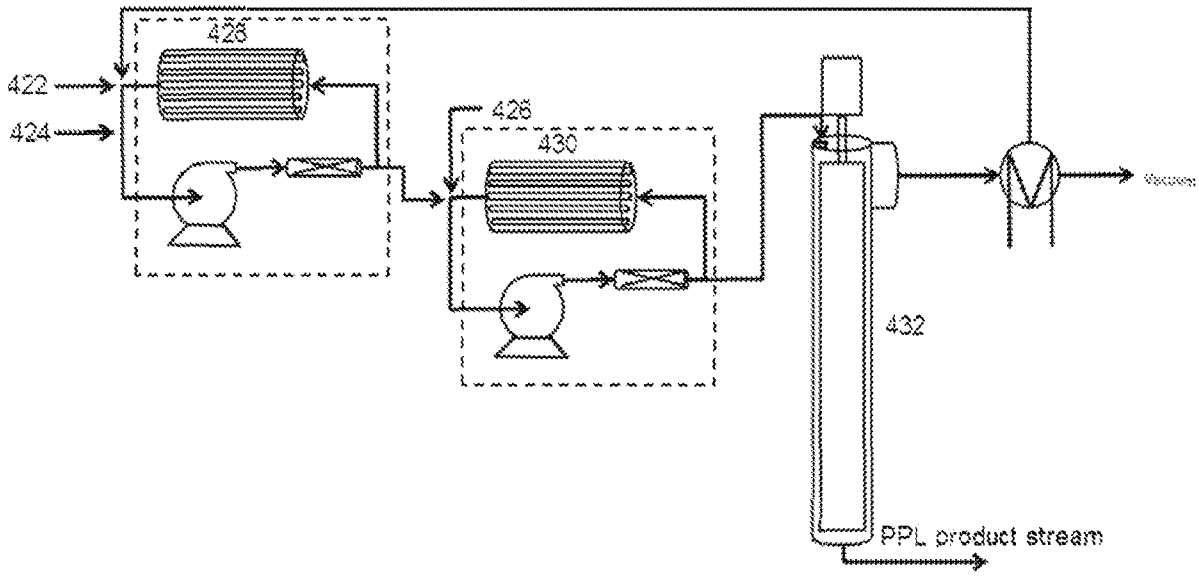

422
424
428
426
430
432
PPL product stream

FIG. 4B

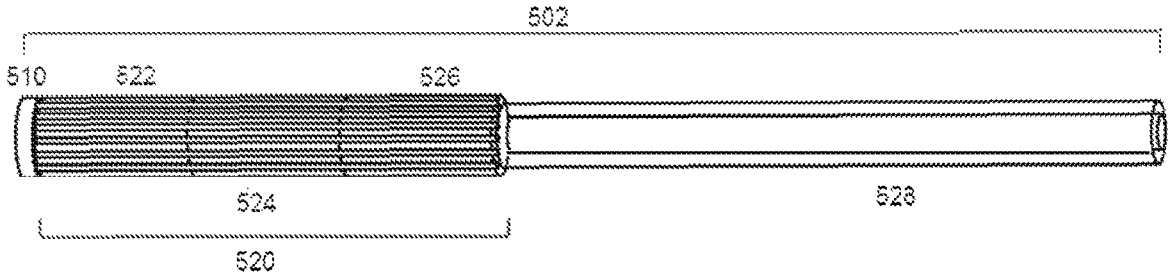

502
510
522
526
524
528
520

FIG. 5

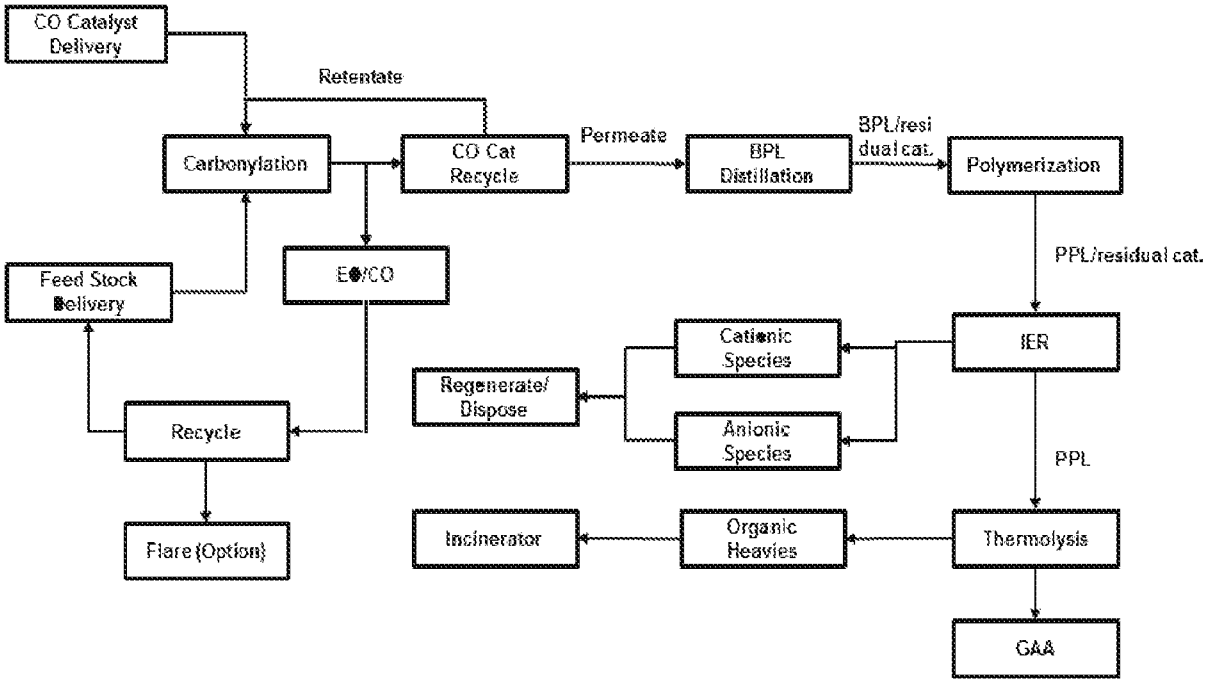

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
PPL/residual cat.
Feed Stock Delivery
EO/CO
Cationic Species
IER
Regenerate/ Dispose
Anionic Species
Recycle
PPL
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
GAA

FIG. 6

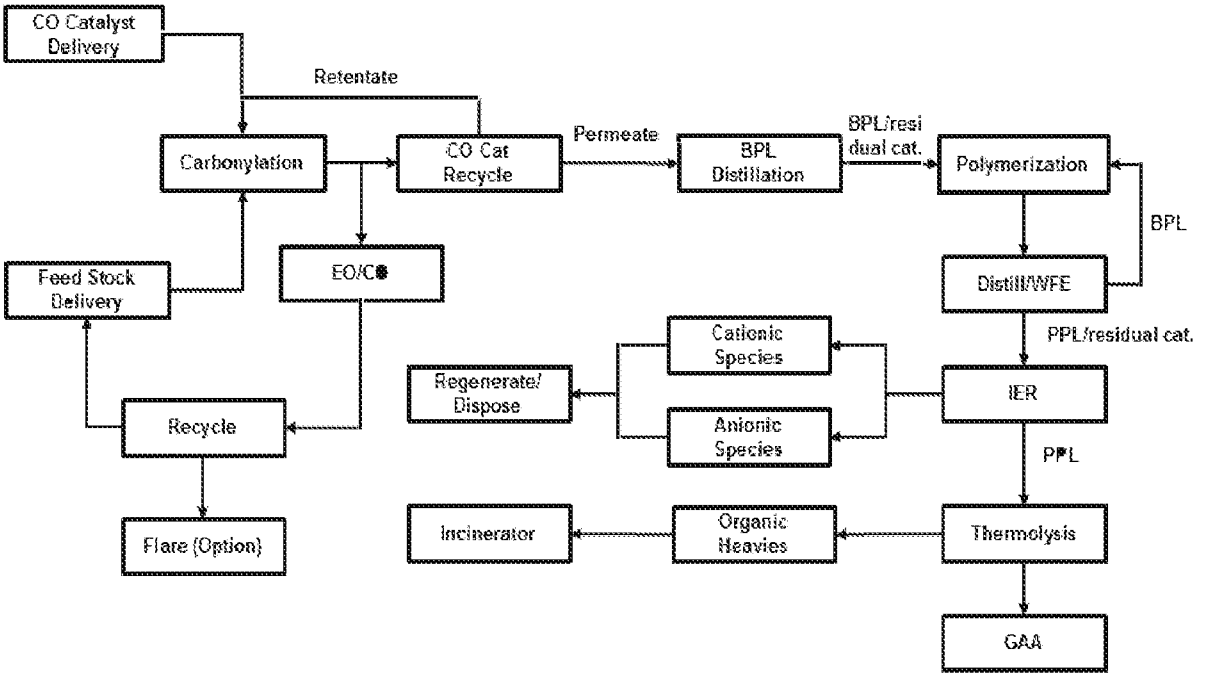

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Cationic Species
Regenerate/ Dispose
IER
Anionic Species
Recycle
PPL
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
GAA

FIG. 7

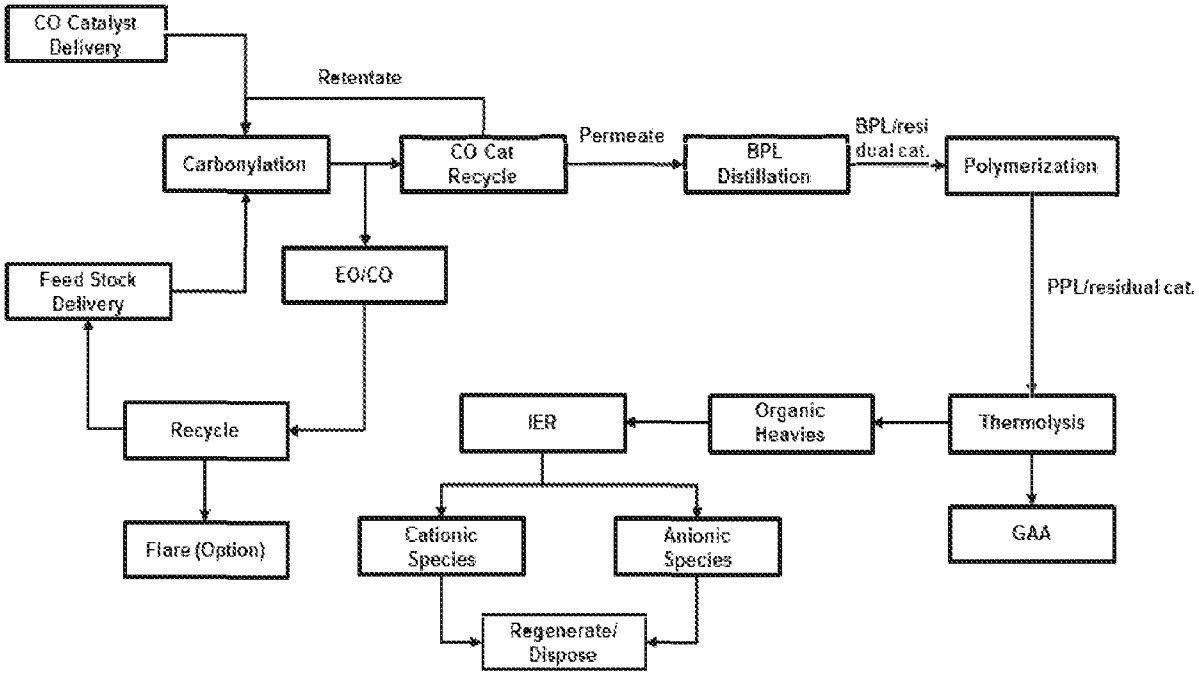

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
Feed Stock Delivery
EO/CO
PPL/residual cat.
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose

FIG. 8

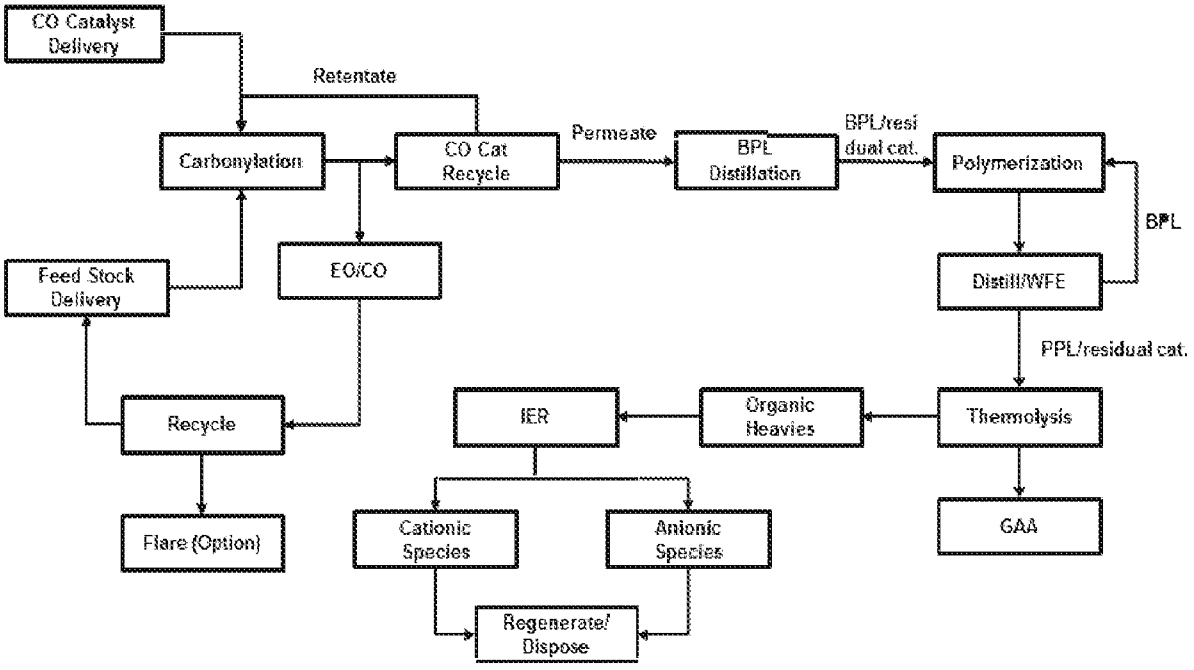

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose

FIG. 9

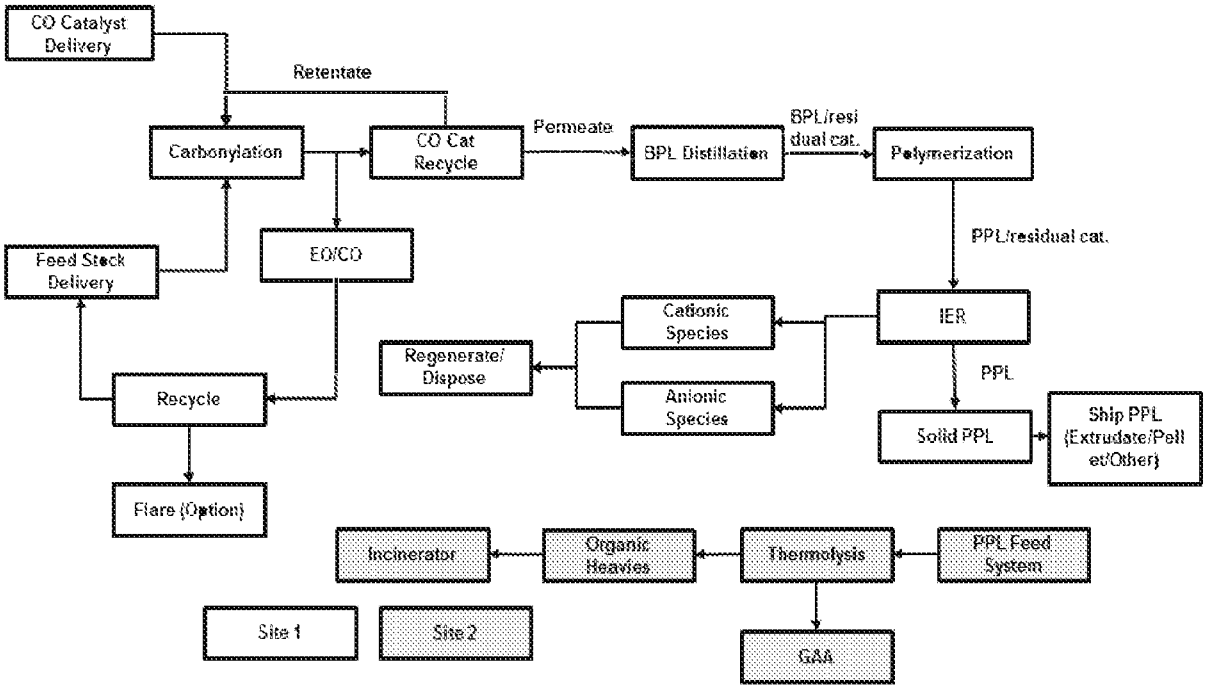

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
PPL/residual cat.
Feed Stock Delivery
EO/CO
Cationic Species
IER
Regenerate/ Dispose
Anionic Species
PPL
Recycle
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
PPL Feed System
Site 1
Site 2
GAA

FIG. 10

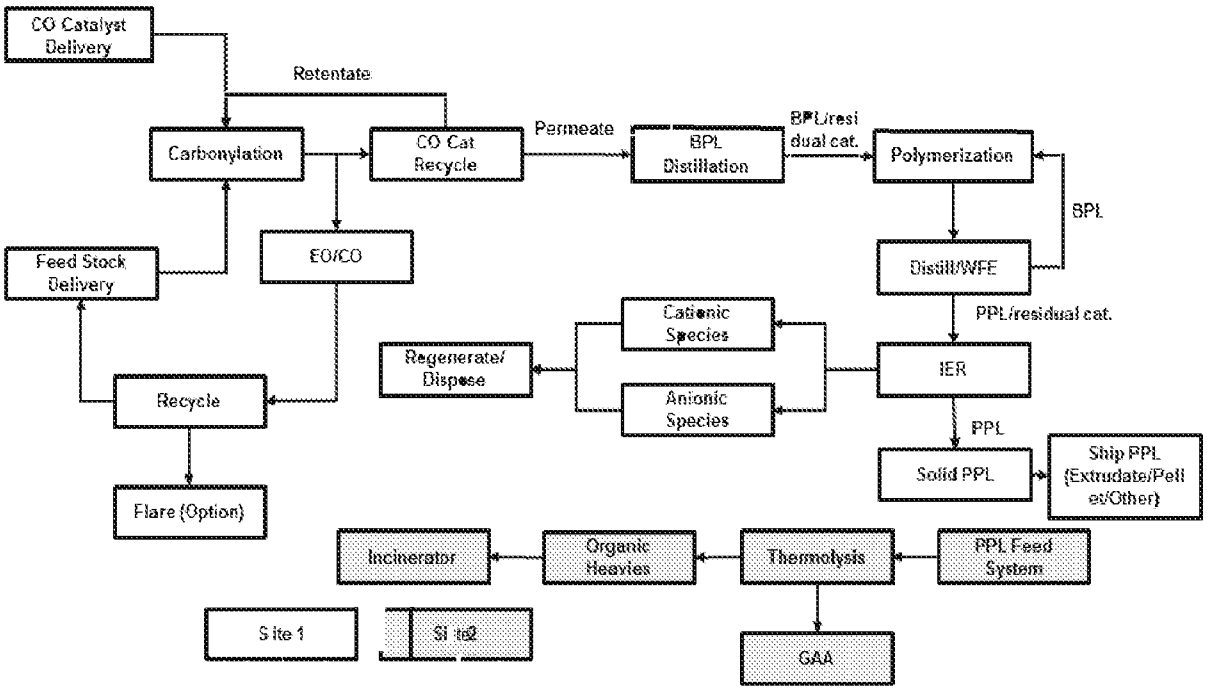

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/residual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Cationic Species
Regenerate/ Dispose
IER
Anionic Species
PPL
Recycle
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Flare (Option)
Incinerator
Organic Heavies
Thermolysis
PPL Feed System
Site 1
Site 2
GAA

FIG. 11

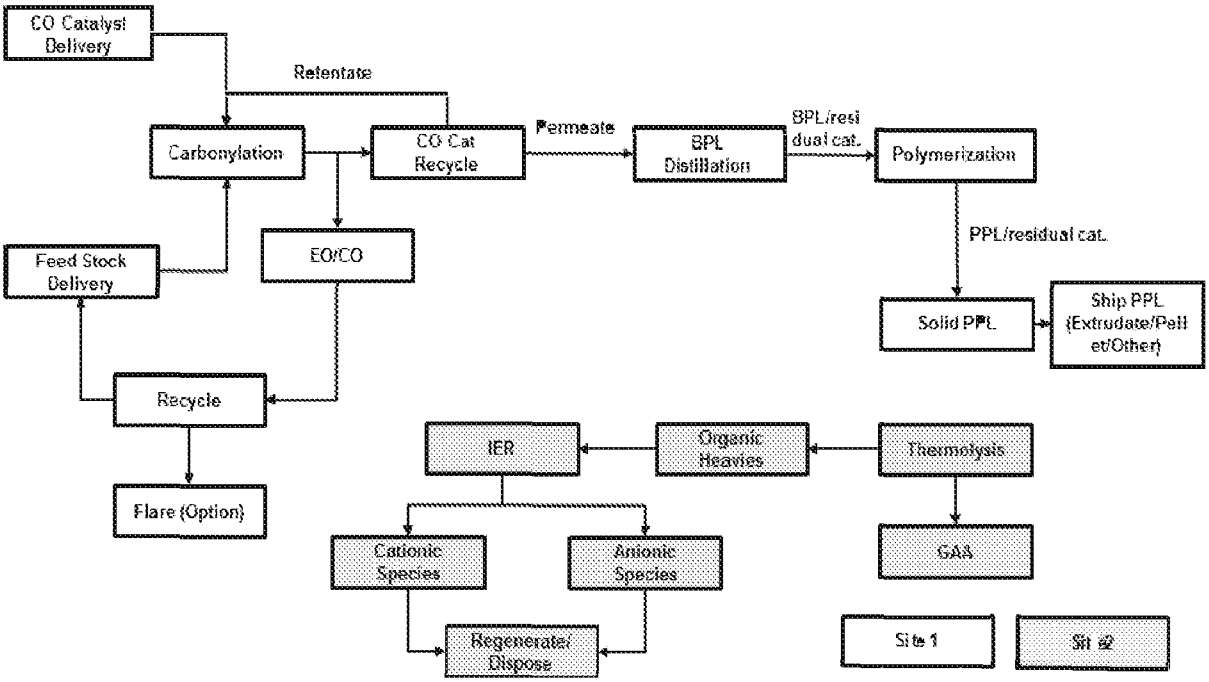

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/resi dual cat.
Polymerization
PPL/residual cat.
Feed Stock Delivery
EO/CO
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose
Site 1
Site 2

FIG. 12

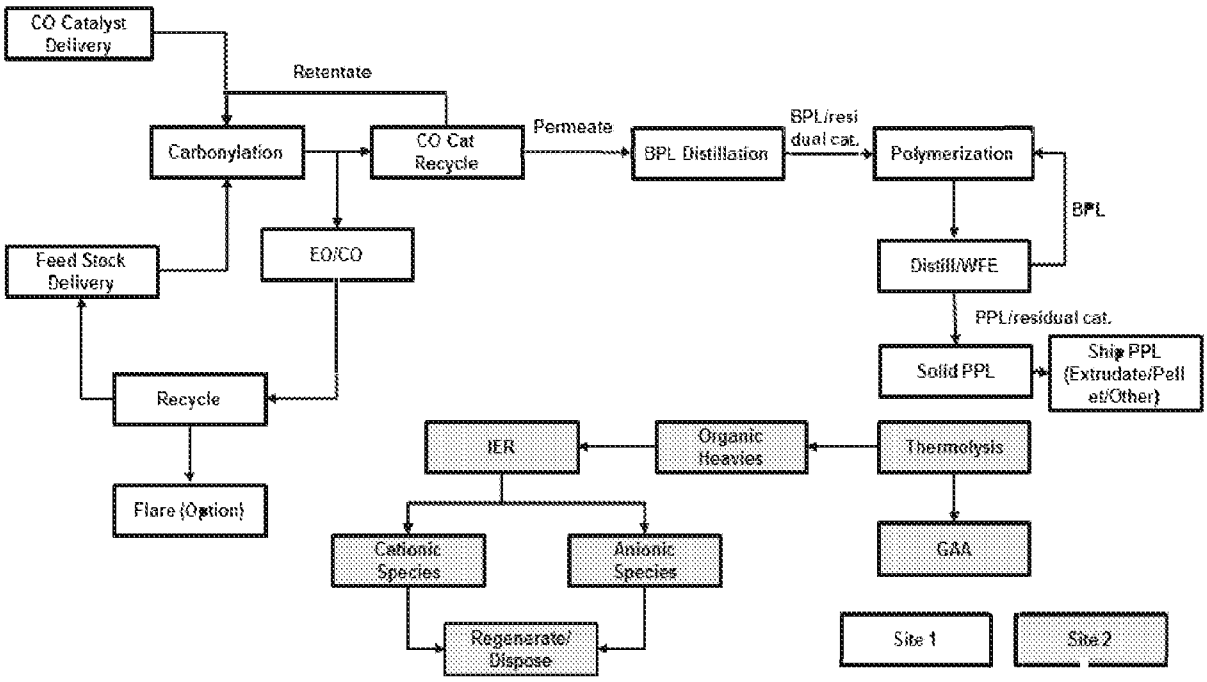

CO Catalyst Delivery
Retentate
Carbonylation
CO Cat Recycle
Permeate
BPL Distillation
BPL/resi dual cat.
Polymerization
BPL
Feed Stock Delivery
EO/CO
Distill/WFE
PPL/residual cat.
Solid PPL
Ship PPL (Extrudate/Pellet/Other)
Recycle
IER
Organic Heavies
Thermolysis
Flare (Option)
Cationic Species
Anionic Species
GAA
Regenerate/ Dispose
Site 1
Site 2

FIG. 13

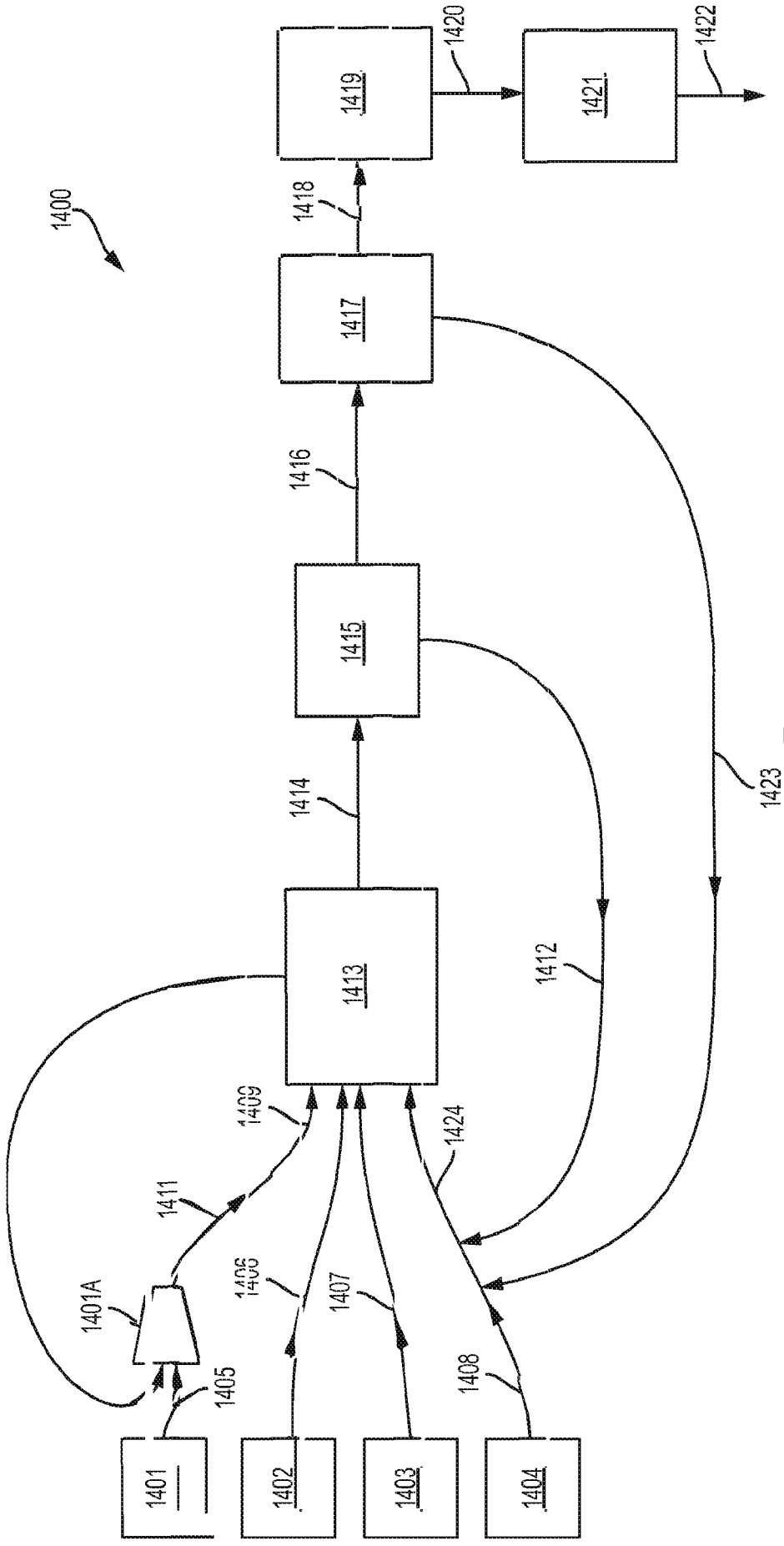

1400
1401
1402
1403
1404
1405
1401A
1406
1407
1408
1409
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424

FIG.14

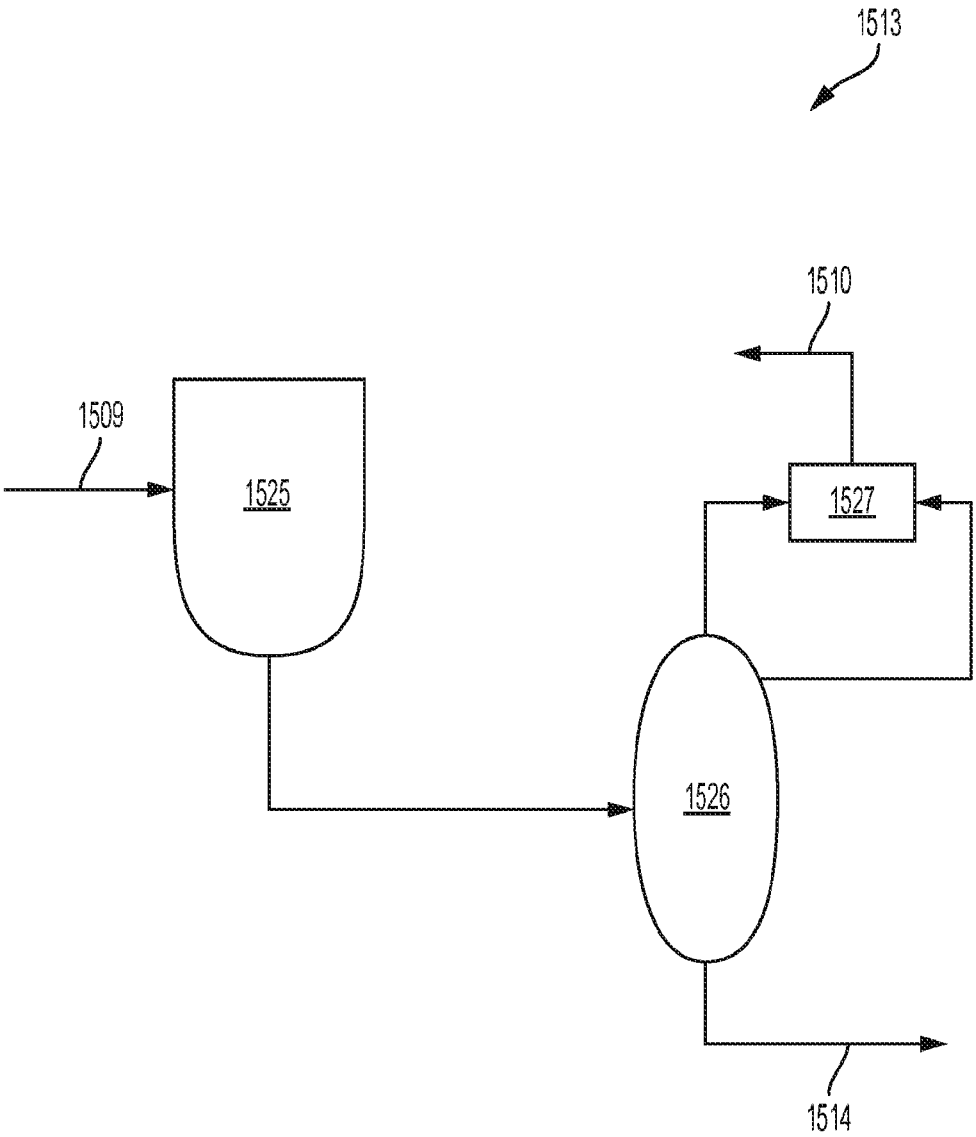


FIG.15

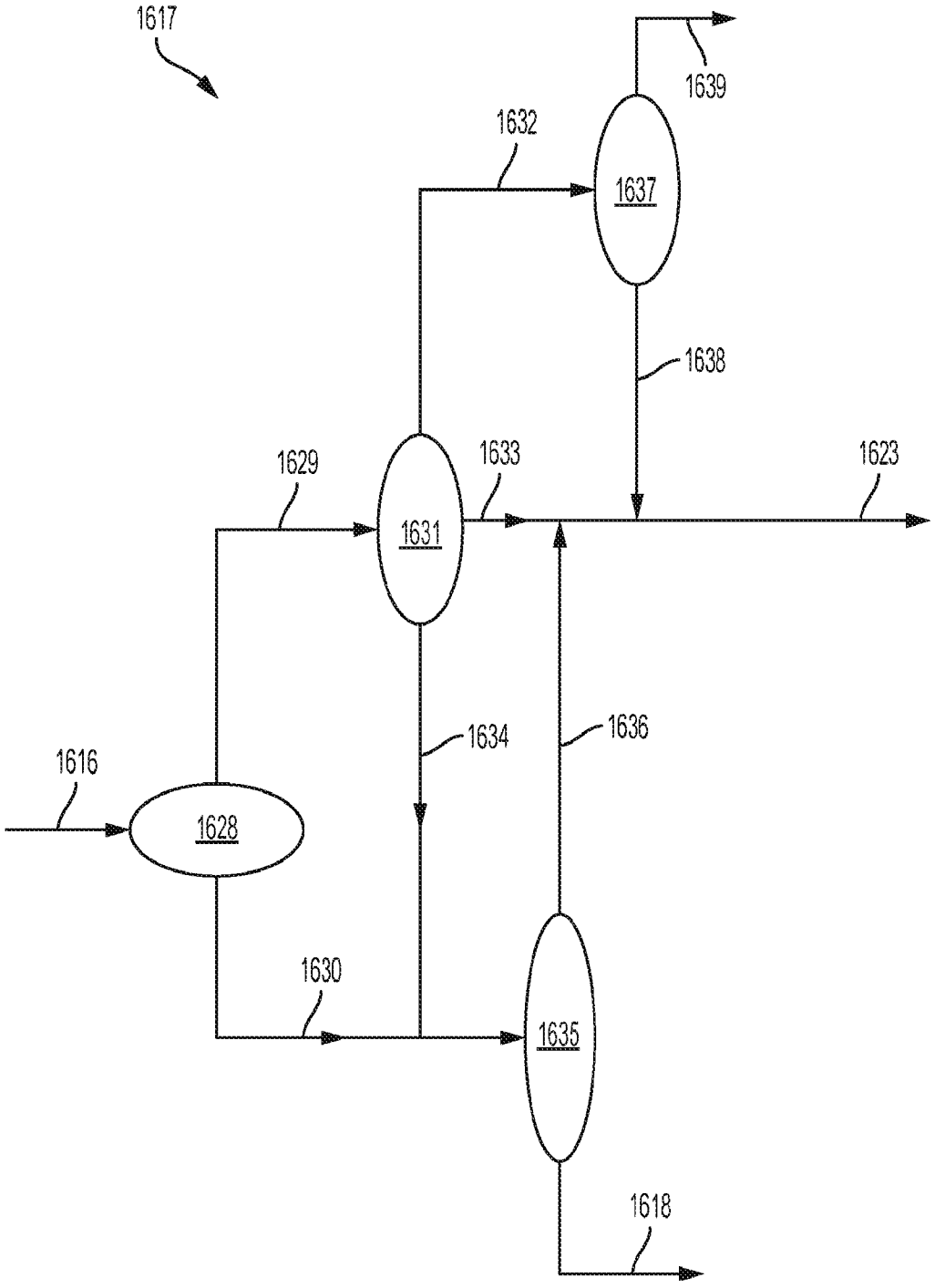

1617
1639
1632
1637
1638
1629
1633
1623
1631
1634
1636
1616
1628
1630
1635
1618

FIG.16

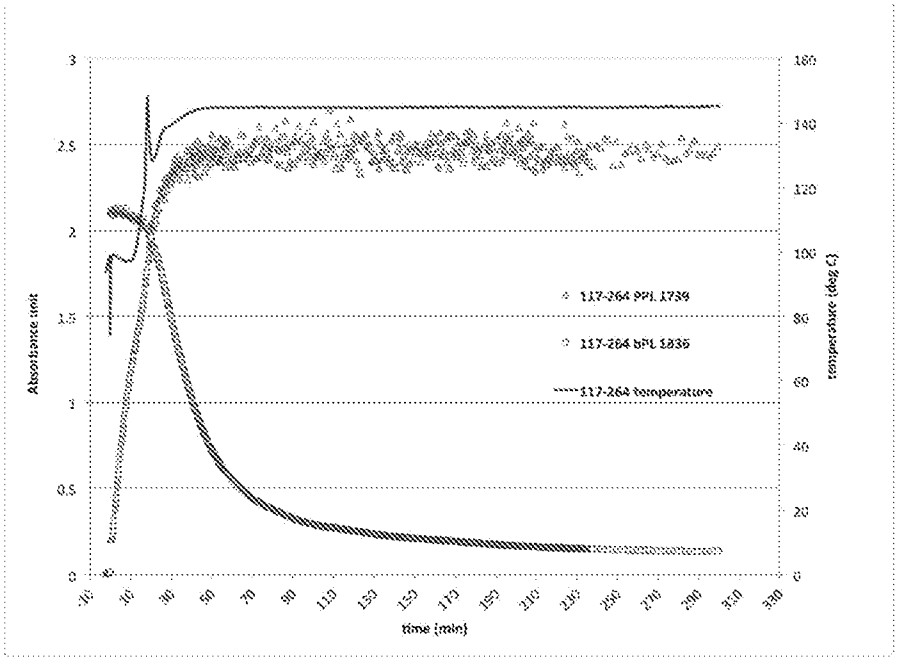

Absorbance unit
temperature (deg C)
time (min)
117-264 PPL 1736
117-264 bPL 1836
117-264 temperature

FIG. 17

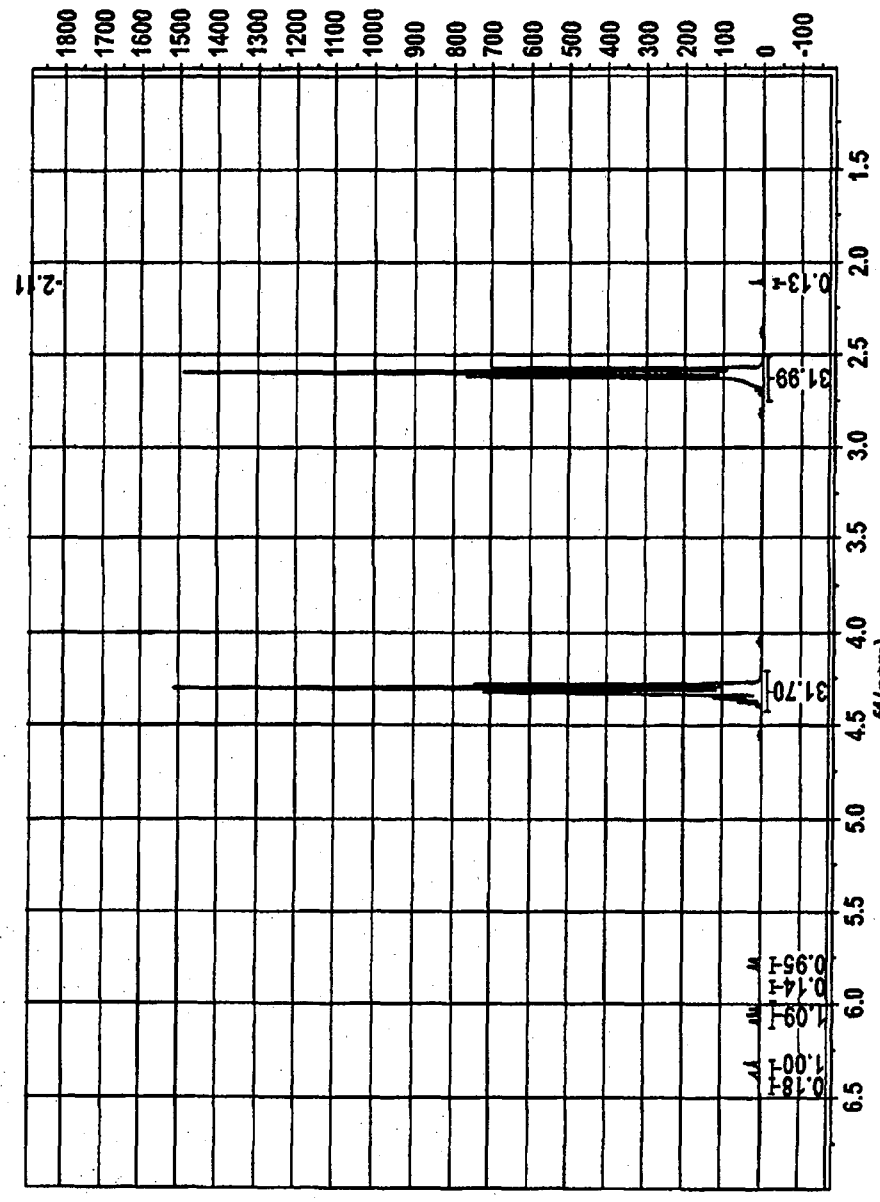

1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1(ppm)
-2.11
0.13
31.99
31.70
0.95
0.14
1.09
1.00
0.18

FIG. 18

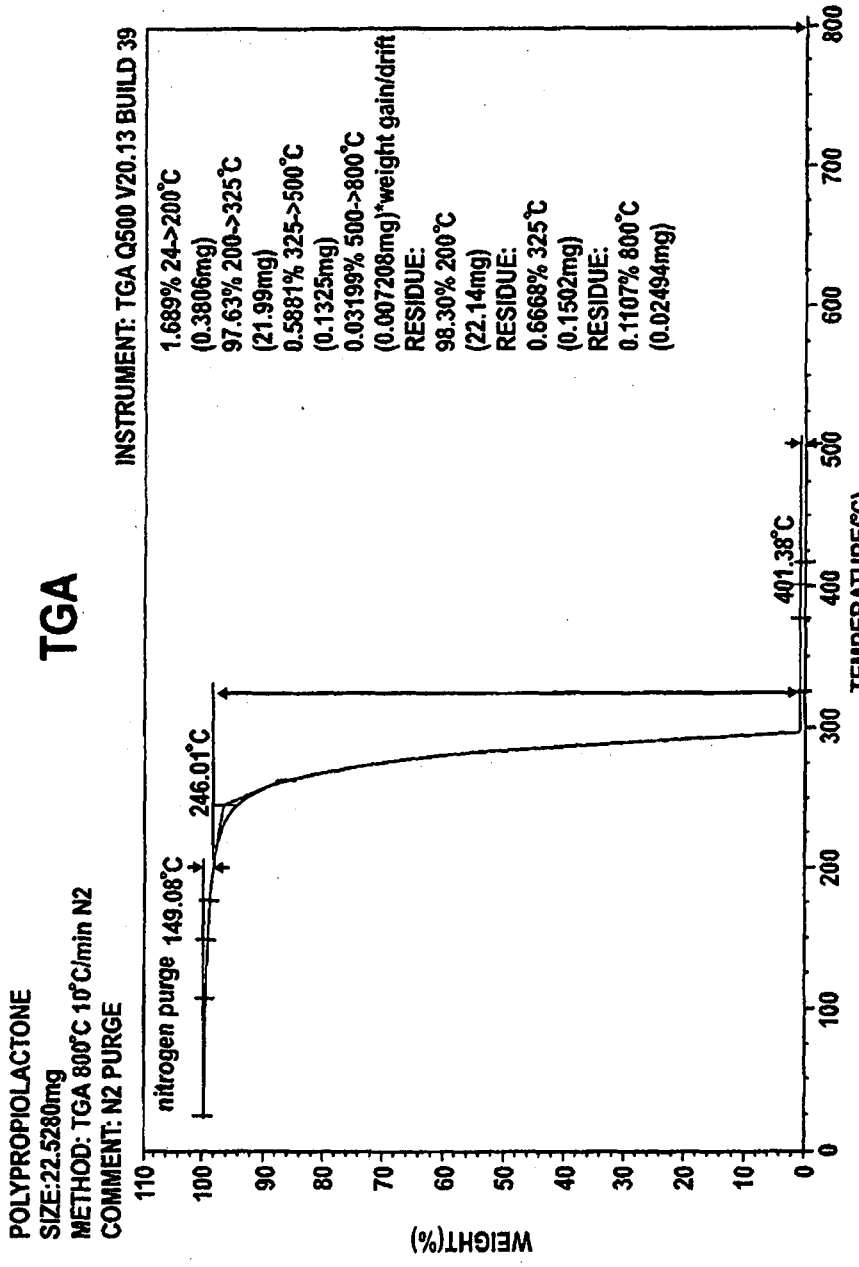

TGA
POLYPROPIOLACTONE
SIZE:22.5280mg
METHOD: TGA 800°C 10°C/min N2
COMMENT: N2 PURGE
INSTRUMENT: TGA Q500 V20.13 BUILD 39
nitrogen purge
149.08°C
246.01°C
401.38°C
1.689% 24->200°C
(0.3806mg)
97.63% 200->325°C
(21.99mg)
0.5881% 325->500°C
(0.1325mg)
0.03199% 500->800°C
(0.007208mg)*weight gain/drift
RESIDUE:
98.30% 200°C
(22.14mg)
RESIDUE:
0.6668% 325°C
(0.1502mg)
RESIDUE:
0.1107% 800°C
(0.02494mg)
WEIGHT(%)
TEMPERATURE(°C)
110
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800

FIG. 19

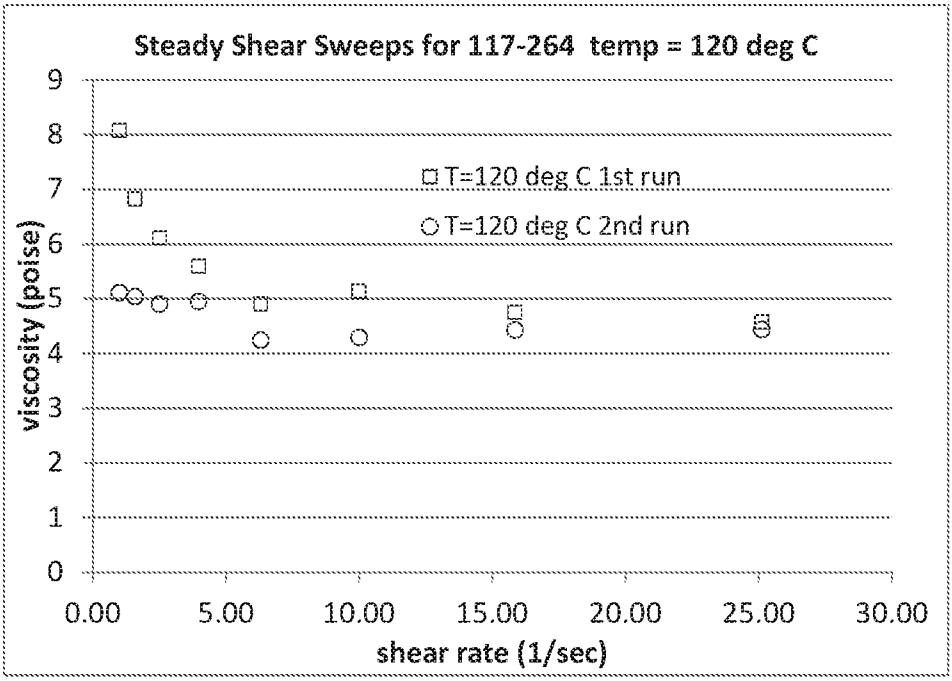

Steady Shear Sweeps for 117-264 temp = 120 deg C
viscosity (poise)
shear rate (1/sec)
T=120 deg C 1st run
T=120 deg C 2nd run
0
1
2
3
4
5
6
7
8
9
0.00
5.00
10.00
15.00
20.00
25.00
30.00

FIG. 20

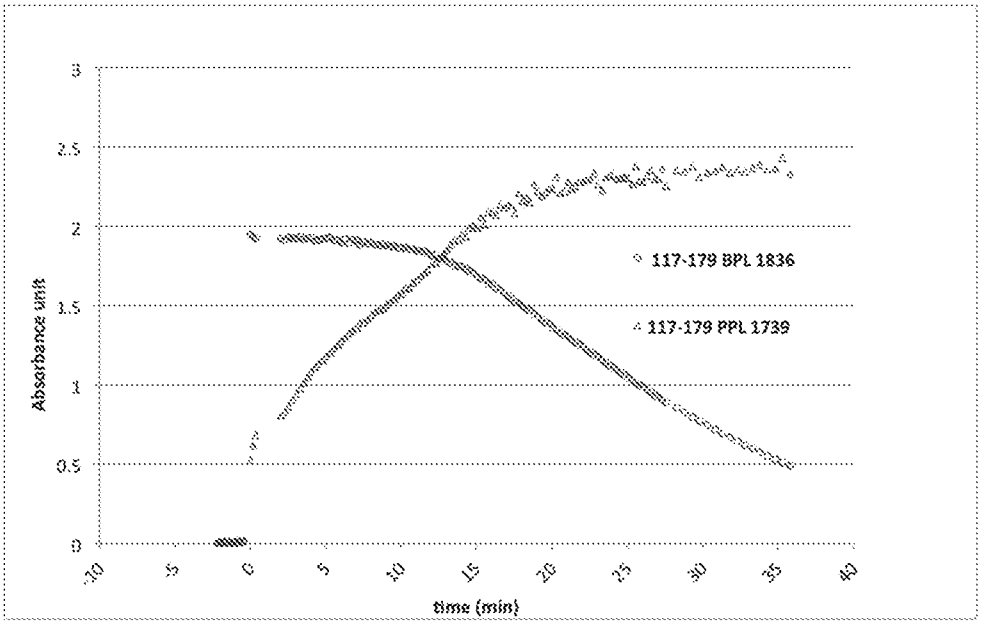


FIG. 21

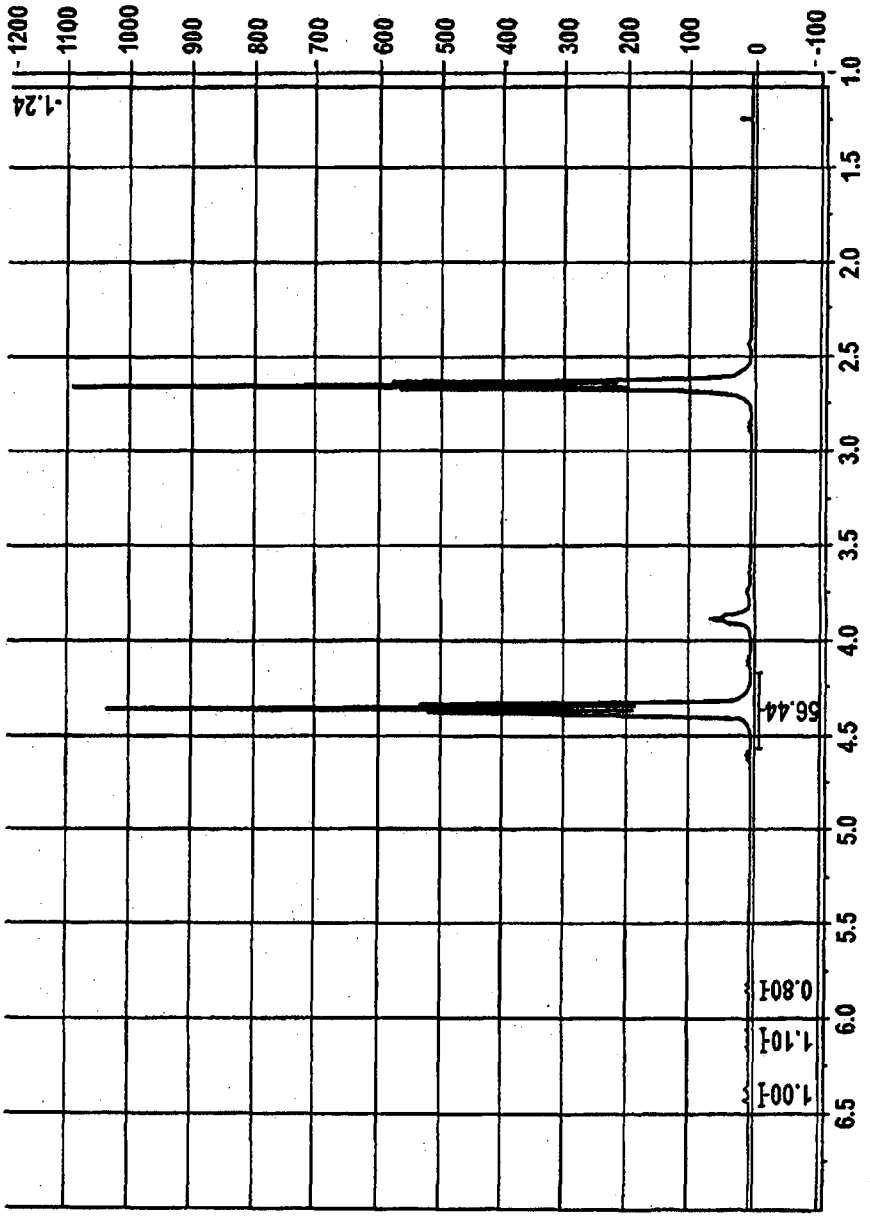

1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
1.24
56.44
0.80
1.10
1.00

FIG. 22

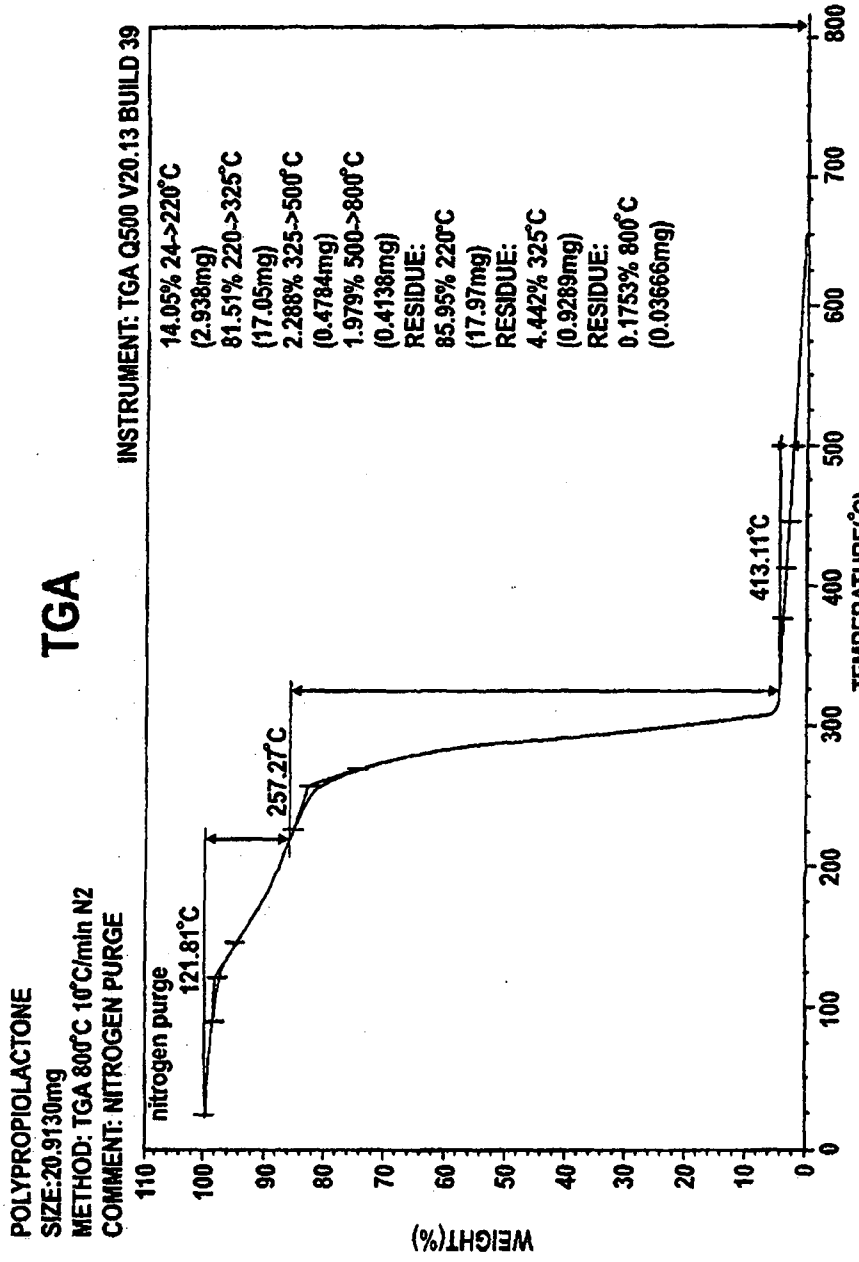


FIG. 23 - REPLACEMENT

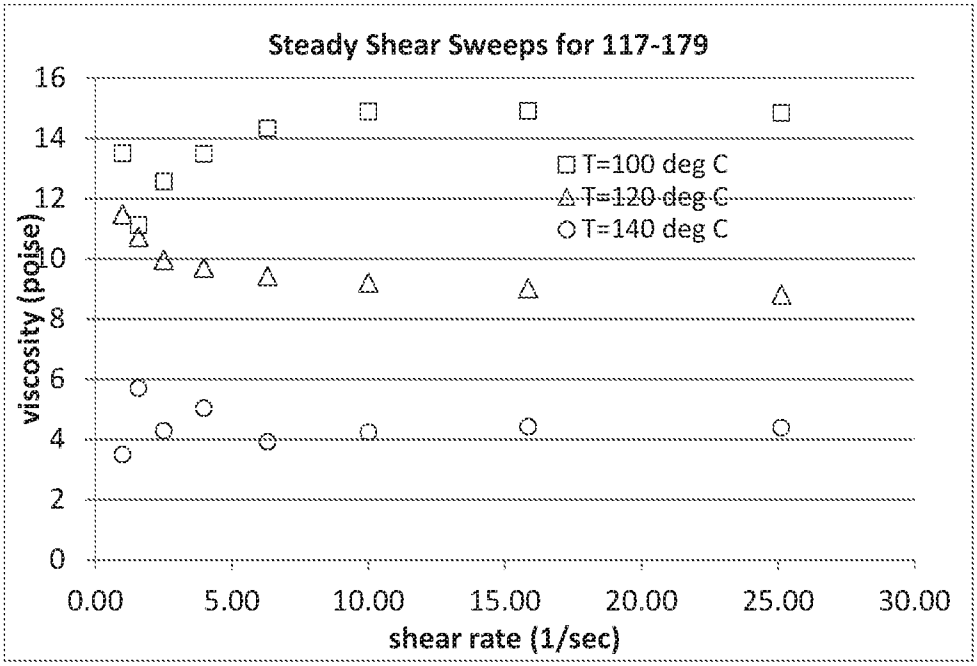
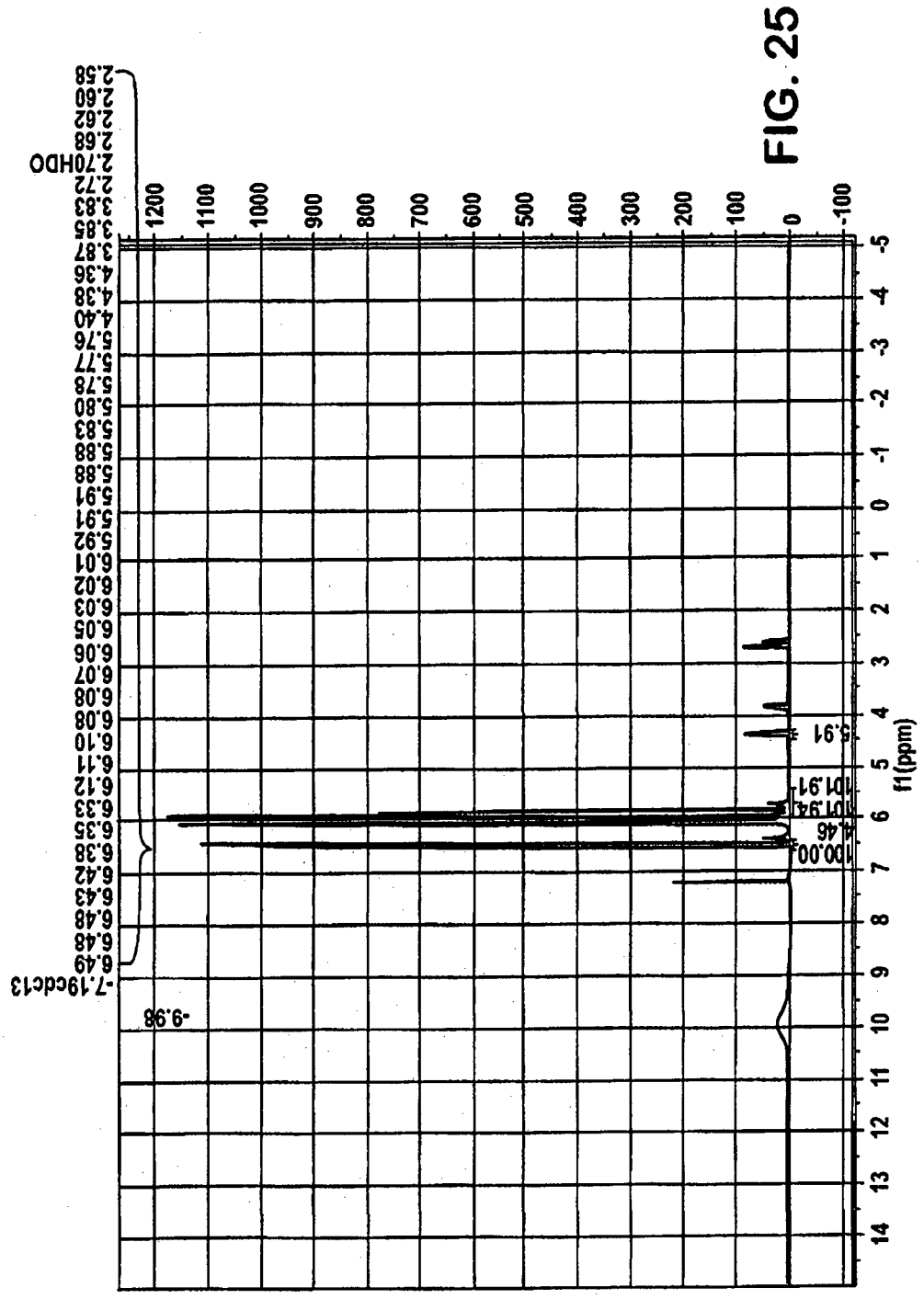

Steady Shear Sweeps for 117-179
viscosity (ppise)
16
14
12
10
8
6
4
2
0
0.00
5.00
10.00
15.00
20.00
25.00
30.00
shear rate (1/sec)
T=100 deg C
T=120 deg C
T=140 deg C

FIG. 24

FIG. 25



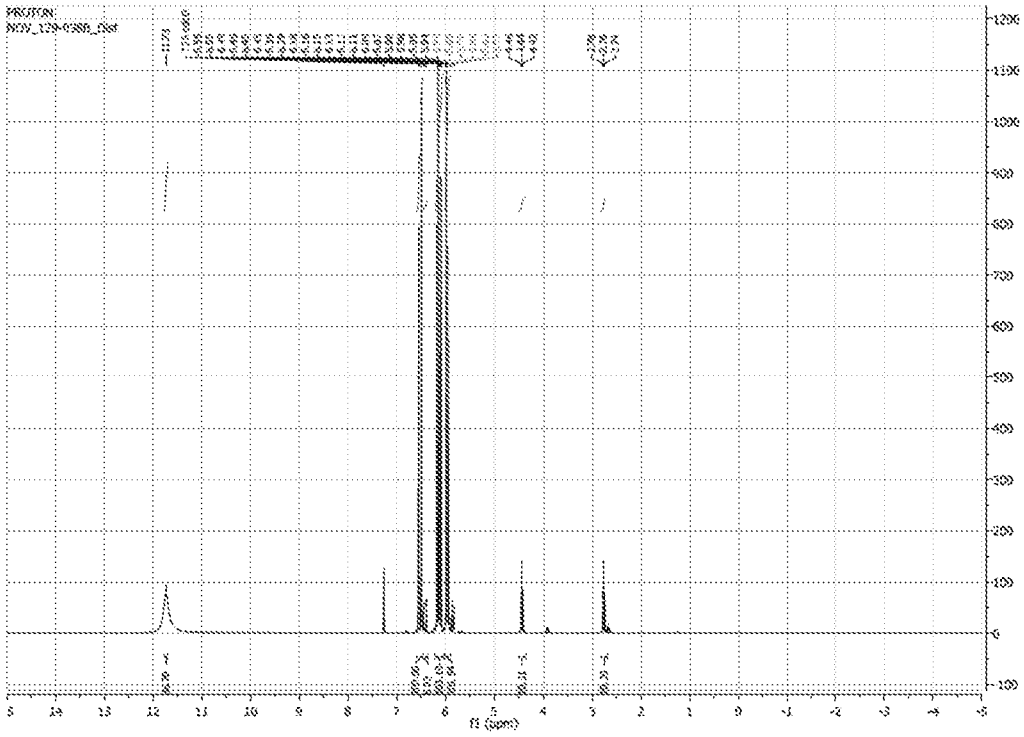


FIG. 26

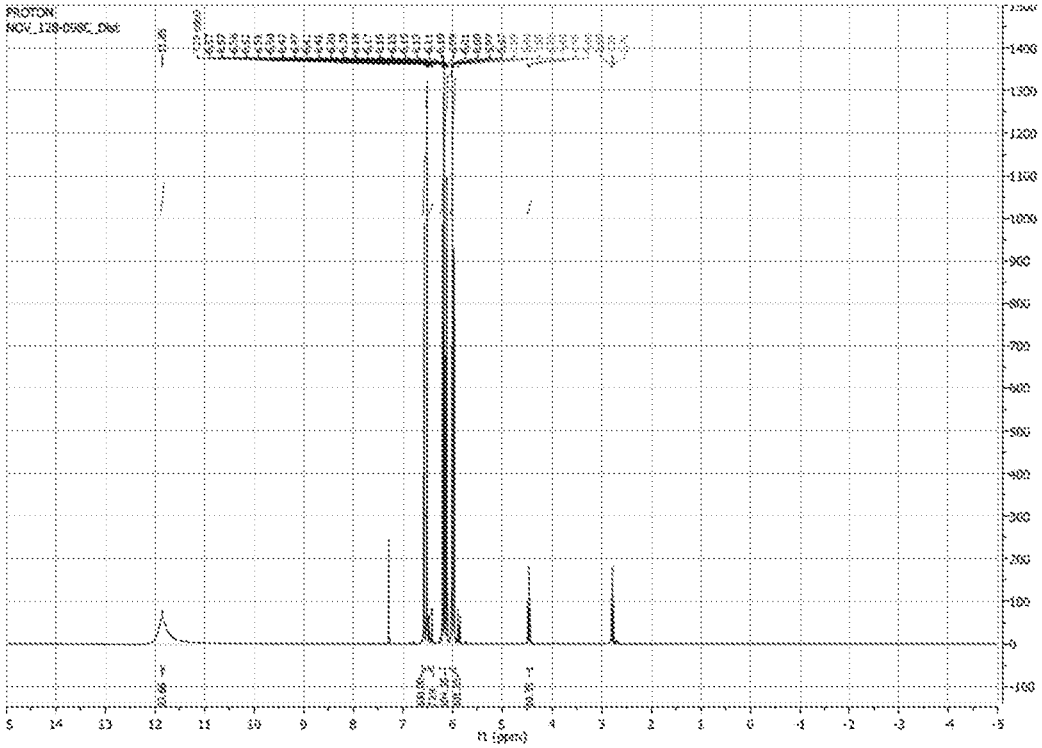


FIG. 27

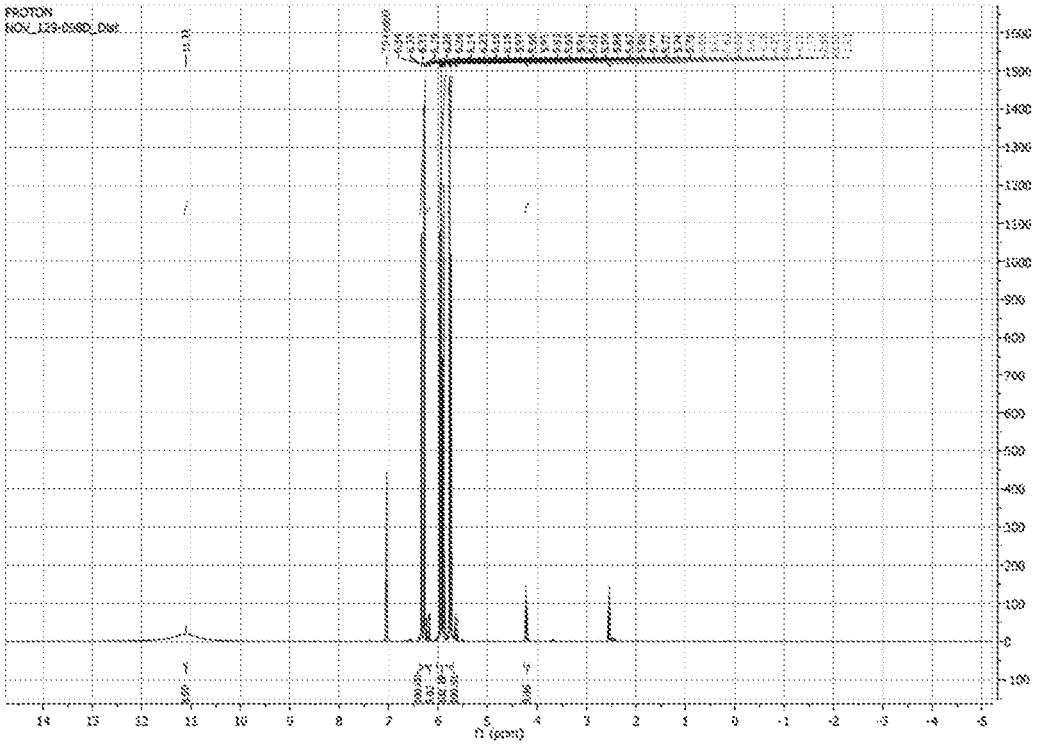


FIG. 28

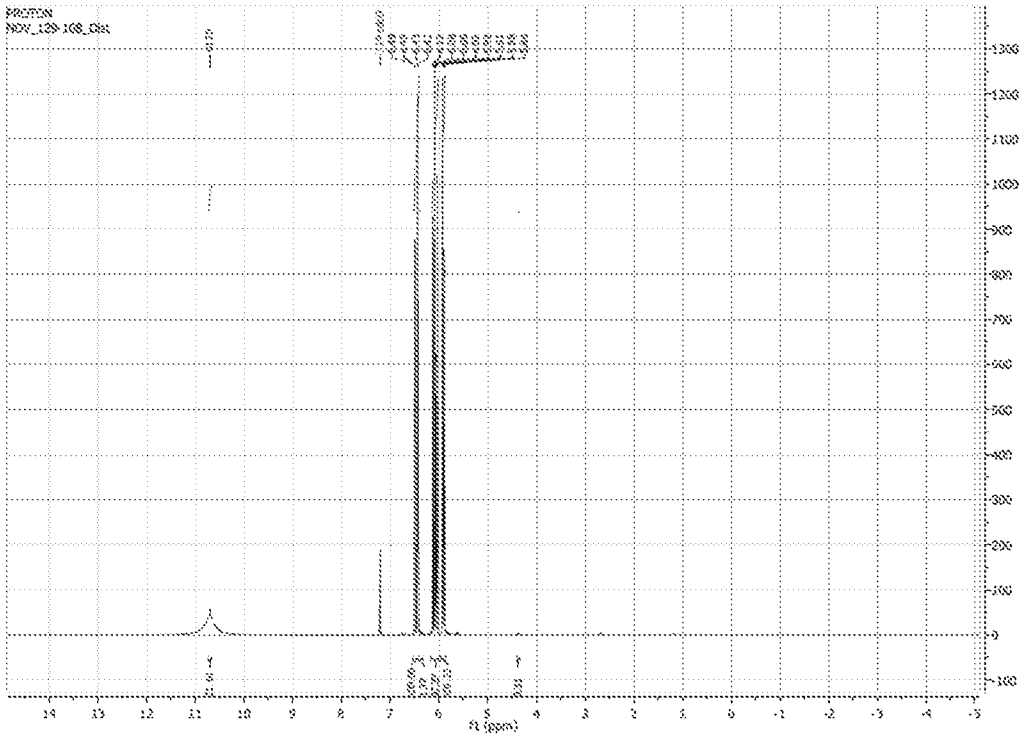


FIG. 29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/044772

A. CLASSIFICATION OF SUBJECT MATTER

C07C 51/09(2006.01)i, C07C 51/12(2006.01)i, C07C 57/04(2006.01)i, C08G 63/08(2006.01)i, C08G 63/82(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C 51/09; C07D 305/12; C07C 67/27; C08G 63/82; C07C 67/30; C07C 57/04; C07C 51/12; C08G 63/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:acrylic acid, polypropiolactone, beta-propiolactone, ethylene oxide, carbon monoxide, carbonylation, polymerization, catalyst, thermolysis, recycle, purification

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013-126375 A1 (NOVOMER, INC.) 29 August 2013 See abstract; and pages 2, 4, 7-15.	27,28
Y		1-3
A		19,23-25,29
Y	WO 2013-185009 A1 (METABOLIX, INC.) 12 December 2013 See abstract; claim 59; and paragraphs [0061], [0072].	1-3
X	US 2014-0275575 A1 (NOVOMER, INC.) 18 September 2014 See abstract; and paragraphs [0003], [0004], [0014], [0049], [0050], [0072], [169], [0191], [0192].	29
Y		2
A	WO 2014-008232 A2 (NOVOMER, INC.) 09 January 2014 See abstract; and pages 2, 16, 17-19.	1-3,19,23-25,27-29
A	WO 2014-004858 A1 (NOVOMER, INC.) 03 January 2014 See the whole document.	1-3,19,23-25,27-29

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 November 2016 (08.11.2016)	**08 November 2016 (08.11.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
CHO, Han Sol
Telephone No. +82-42-481-5580

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/044772

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 6, 18
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 6 and 18 refer to an unsearchable claim which is not drafted in accordance with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4, 5, 7-17, 19(1), 20-22, 26
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/044772

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
L	International Application No. PCT/US2016/044927 filed on 29 July 2016 * Said application filed by the same applicant with the same priority (US 62/199,918 on 31 July 2015) comprises identical claims to those of this application. * Claim 19 found twice in this application and thus the second one was degignated as claim 19(1) by this Authority.	1-3,19,23-25,27-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/044772

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013-126375 A1	29/08/2013	AU 2013-222568 A1	11/09/2014
		CA 2864750 A1	29/08/2013
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(12)发明专利申请

(10)申请公布号 CN 108026013 A
(43)申请公布日 2018.05.11

(21)申请号 201680055982.1

(22)申请日 2016.07.29

(30)优先权数据
62/199,918 2015.07.31 US

(85)PCT国际申请进入国家阶段日
2018.03.26

(86)PCT国际申请的申请数据
PCT/US2016/044772 2016.07.29

(87)PCT国际申请的公布数据
WO2017/023777 EN 2017.02.09

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(51)Int.Cl.
C07C 51/09(2006.01)
C07C 51/12(2006.01)
C07C 57/04(2006.01)
C08G 63/08(2006.01)
C08G 63/82(2006.01)

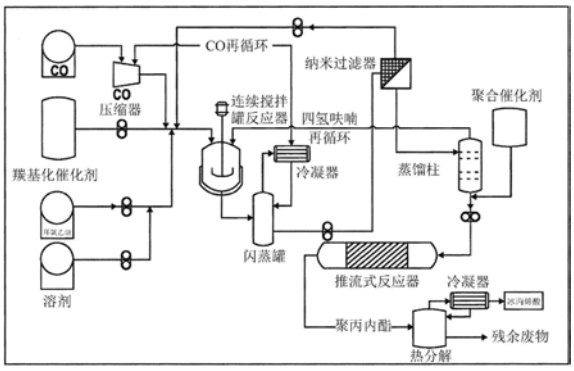
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(54)发明名称

用于丙烯酸及其前体的生产系统/生产方法

(57)摘要

本文提供用于按工业规模利用环氧乙烷和一氧化碳产生丙烯酸的系统，以及使用这些系统的方法。所述生产系统/生产方法具有各种单元操作，例如，包括：配置成利用环氧乙烷和一氧化碳生产β-丙内酯的β-丙内酯生产系统/生产方法；配置成利用β-丙内酯生产聚丙内酯的聚丙内酯生产系统/生产方法；和配置成通过聚丙内酯的热分解生产具有高纯度的丙烯酸的冰丙烯酸生产系统/生产方法。



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1.一种用于利用β-丙内酯源产生丙烯酸的方法,其包括:

在具有至少一个聚合反应器的聚丙内酯反应区中使包括β-丙内酯的BPL进料流与聚合引发剂接触,所述至少一个聚合反应器产生包括聚丙内酯和β-丙内酯的聚丙内酯出口流;及

将所述聚丙内酯出口流的至少一部分传送到包括热分解反应器的丙烯酸产生区,所述热分解反应器接收所述聚丙内酯出口流的所述至少一部分且产生包括丙烯酸的丙烯酸流。

2.根据权利要求1所述的方法,其中所述BPL进料流中的所述β-丙内酯的源是从环氧乙烷和一氧化碳通过以下方式制得:

在羰基化反应区中使包括一氧化碳进料、环氧乙烷进料和催化剂再循环流的输入组分与羰基化催化剂和溶剂接触,且产生包括β-丙内酯、环氧乙烷和羰基化催化剂的BPL出口流;

将所述BPL出口流的至少一部分传送到羰基化催化剂再循环区且将所述部分分离成:i)BPL分离流,其包括所述BPL出口流的一部分,至少一些羰基化催化剂已经从所述BPL出口流移除;和ii)所述再循环流,其包括β-丙内酯、溶剂、环氧乙烷、羰基化催化剂、丁二酸酐和乙醛;

将所述再循环流的至少一部分传送到所述羰基化反应区;

在包括至少一个分离器的BPL纯化区中纯化所述BPL分离流的至少一部分,其中所述BPL纯化区产生纯化BPL流且在一或多个排出流中排出β-丙内酯的一部分且排出溶剂、环氧乙烷以及羰基化催化剂、丁二酸酐和乙醛,所述排出流包括β-丙内酯、溶剂、环氧乙烷以及羰基化催化剂、丁二酸酐和乙醛中的至少一种;及,将所述纯化BPL流的至少一部分传送到所述聚丙内酯反应区。

3.根据权利要求1或2所述的方法,其中所述聚合引发剂选自由以下组成的群组:季铵盐、羧酸的碱金属盐、丙烯酸铵、乙酸铵、丙烯酸鏻、鏻盐、丙烯酸钠、丙烯酸钾、乙酸鏻、四正丁基丙烯酸铵、乙酸钠、乙酸钾、四正丁基乙酸铵、三甲基苯基丙烯酸铵、三甲基苯基乙酸铵或四苯基丙烯酸鏻且所述聚丙内酯反应区中存在自由基聚合抑制剂。

4.根据权利要求1到3中任一权利要求所述的方法,其中所述自由基聚合抑制剂包括吩噻嗪,优选地浓度为50到500ppmw且更优选地浓度为150到250ppm。

5.根据权利要求1到4中任一权利要求所述的方法,其中所述聚丙内酯反应器区包括第一聚合反应器和第二聚合反应器;所述第一聚合反应器产生包括聚丙内酯、β-丙内酯和聚合引发剂的中间混合物;所述中间混合物和其它聚合引发剂传送到产生所述聚丙内酯出口流的至少一部分的所述第二聚合反应器;且所述聚丙内酯出口流的至少一部分包括聚丙内酯、β-丙内酯和聚合引发剂。

6.根据权利要求5所述的方法,其中聚丙内酯与在第二反应区制得的所述聚丙内酯出口流的所述部分在由蒸发器、闪蒸罐蒸发器、刮膜式蒸发器或蒸馏设备中的至少一个中分离。

7.根据权利要求1到6中任一权利要求所述的方法,其中所述聚丙内酯出口流包括固体聚丙内酯。

8.根据权利要求1到7中任一权利要求所述的方法,其中所述至少一个聚合反应区含有连续反应器、半间歇式反应器、连续流动搅拌罐反应器、环流反应器或推流式反应器中的至

少一个，且丙烯酸反应区包括用于接收熔化的丙内酯的热分解反应器，且所述热分解反应器呈连续搅拌罐反应器、推流式反应器、刮膜式蒸发器、移动床反应器、捏合式反应器和流化床反应器的形式。

9.根据权利要求1到8中任一权利要求所述的方法，其中所述丙烯酸流的至少一部分分离成(i)丙烯酸流，其包括具有至少90％纯度的丙烯酸，和(ii)有机重物质流。

10.根据权利要求2到8中任一权利要求所述的方法，其中所述BPL纯化区产生作为所述排出流中的一个的EO排出流，所述EO排出流包括环氧乙烷且所述EO排出的至少一部分传送到所述羰基化反应区。

11.根据权利要求2到10中任一权利要求所述的方法，其中所述BPL纯化区产生作为所述EO排出流中的一个的溶剂回收流，所述溶剂回收流包括溶剂，所述溶剂回收流的至少一部分传送到所述羰基化反应区。

12.根据权利要求2到11中任一权利要求所述的方法，其中I)所述羰基化催化剂再循环区包括一或多个膜系统，从所述一或多个膜系统回收所述催化剂再循环液流作为保留物且回收BPL分离流作为渗透物；且II)所述BPL纯化区包括a.)包括至少一个蒸馏柱的EO回收段，其接收所述BPL分离流的至少一部分且产生含有传送到所述羰化反应器的环氧乙烷的EO流和含有溶剂和β-丙内酯的溶剂底部物流，b.)包括至少一个蒸馏柱的溶剂回收段，其接收所述溶剂底部物流的至少一部分且产生传送到所述羰基化区的包括溶剂的顶部回收溶剂流和包括β-丙内酯的BPL底部物流，和c.)包括至少一个蒸馏柱的BPL浓缩段，其接收所述BPL底部物流且产生底部排出流且产生所述纯化BPL作为顶部物流。

13.根据权利要求2到12中任一权利要求所述的方法，其中所述羰基化催化剂是以下各项的至少一种：钴铝催化剂；与铝卟啉化合物组合的羰基钴酸盐、与铝沙仑化合物组合的羰基钴酸盐、与铝柳酰醋氨酚化合物组合的羰基钴酸盐和Al(TPP)Co(CO)$_4$。

14.根据权利要求2到13中任一权利要求所述的方法，其中所述羰基化催化剂至少部分溶解于催化剂溶剂中，且所述溶剂包括醚、烃、四氢呋喃、己烷、2,5-二甲基四氢呋喃、环丁砜、N-甲基吡咯烷酮、1,3-二甲基-2-咪唑啉酮、二乙二醇二甲醚、三乙二醇二甲醚、四乙二醇二甲醚、二乙二醇二丁醚、异山梨醇醚、甲基叔丁基醚、二乙醚、二苯醚、1,4-二恶烷、碳酸亚乙酯、碳酸亚丙酯、碳酸亚丁酯、二元酯、二乙醚、乙腈、乙酸乙酯、乙酸丙酯、乙酸丁酯、2-丁酮、环己酮、甲苯、二氟苯、二甲氧基乙烷、丙酮和甲基乙基酮中的至少一种。

15.根据权利要求2到14中任一权利要求所述的方法，其中所述羰基化反应区：包含反应器操作条件，温度从-20℃到160℃且压力从100psig到5000psig；至少一个反应器，其选自由连续反应器或半间歇式反应器、连续流动搅拌罐反应器或环流反应器组成的群组；且以至少90％且优选地至少99％的选择性产生β-丙内酯。

16.根据权利要求2到15所述的方法，其中所述BPL出口流按质量分数计满足以下条件，具有：至少0.1且至多0.4β-丙内酯；至少0.且至多0.9溶剂；至少0.005且至多0.07环氧乙烷；0.0005到0.001之间的一氧化碳；至少0.0001且至多0.005催化剂；至少0.0001且至多0.06乙醛；或至少0.0001且至多0.06丁二酸酐。

17.根据权利要求2到16中任一权利要求所述的方法，其中所述BPL浓缩段包含真空柱且回收所述纯化BPL流作为真空柱顶部物流，所述真空柱顶部物流具有纯度是至少99％且优选地至少99.5％且最优选地99.9％的β-丙内酯。

19.一种用于利用环氧乙烷和一氧化碳产生丙烯酸的方法,其包括:

在羰基化反应区中使一氧化碳进料、环氧乙烷进料、CO顶部物流和BPL再循环流与羰基化催化剂和溶剂接触,且产生包括β-丙内酯、溶剂、环氧乙烷、一氧化碳、羰基化催化剂、乙醛和丁二酸酐的BPL出口流;

将所述BPL出口流的至少一部分传送到CO/EO分离器且回收i.)CO分离器顶部物流,其中所述CO分离器顶部物流包括环氧乙烷和一氧化碳,和ii.)CO分离器底部物流,其包括β-丙内酯、溶剂、羰基化催化剂、乙醛、丁二酸酐和环氧乙烷;

将所述CO分离器顶部物流的至少一部分传送到所述羰基化反应区;

将所述CO分离器底部物流的至少一部分传送到羰基化催化剂再循环区的膜分离段,且将所述CO分离器底部物流的所述至少一部分分离成i)包括保留物的BPL再循环流,所述保留物含有分离的羰基化催化剂、溶剂和β-丙内酯,和ii)包括渗透物的BPL分离流,所述渗透物含有β-丙内酯、溶剂、乙醛、丁二酸酐、环氧乙烷和羰基化催化剂;

将所述BPL再循环流的至少一部分传送到所述羰基化反应区;

将所述BPL分离流的至少一部分传送到包括至少一个分离区的BPL纯化区,所述至少一个分离区将所述BPL分离流分离成包括溶剂的溶剂再循环流和包括β-丙内酯和羰基化催化剂的纯化BPL流;

将所述纯化BPL流的至少一部分和聚合引发剂传送到具有至少一个聚合反应器的聚丙内酯反应区,所述至少一个聚合反应器使所述纯化BPL流的所述至少一部分与所述聚合引发剂接触且产生包括聚丙内酯和β-丙内酯的聚丙内酯出口流;

将所述聚丙内酯出口流的至少一部分传送到具有至少一个分离区的PPL/BPL处理区以产生i.)PPL/BPL顶部物流,其相对于所述聚丙内酯出口流增大β-丙内酯的浓度,和ii)PPL/BPL分离器底部物流,其包括聚丙内酯;

将所述PPL/BPL顶部物流的至少一部分传送到所述聚丙内酯反应区;

将所述PPL/BPL底部物流的至少一部分传送到包括热分解反应器的丙烯酸产生区,所述热分解反应器接收所述聚丙内酯出口流的所述至少一部分且产生丙烯酸流;及

在分离器中将所述丙烯酸流的至少一部分分离成(i)丙烯酸流,其包括具有至少90%纯度的丙烯酸,和(ii)有机重物质流。

18.根据权利要求17所述的方法,其中所述丙烯酸流具有纯度大于99.5%的丙烯酸且包括冰丙烯酸。

19.根据权利要求17到18中任一权利要求所述的方法,其中所述至少一个聚合反应器以至少50%的聚丙内酯转化率产生聚丙内酯。

20.根据权利要求17到19中任一权利要求所述的方法,其中所述PPL/BPL处理区中的所述至少一个分离区包括至少一个闪蒸罐和/或至少一个蒸发器,所述至少一个蒸发器包括刮膜式蒸发器、薄膜蒸发器或降膜蒸发器;且所述CO分离器是闪蒸罐。

21.根据权利要求17到20中任一权利要求所述的方法,其中所述羰化反应器区在30℃到160℃之间的温度下且在100psig到5000psig之间的压力下操作,所述至少一个蒸馏柱在处于或低于大气压下且在小于120℃的温度下操作。

22.根据权利要求17到21中任一权利要求所述的方法,其中所述溶剂再循环流包括溶剂和小于15wt%的β-丙内酯、环氧乙烷、一氧化碳、乙醛或丁二酸酐,或其任何组合,且其中

所述纯化BPL流包括(i)β-丙内酯和(ii)小于1wt％的溶剂、环氧乙烷、一氧化碳、乙醛或丁二酸酐，或其任何组合。

23.一种用于利用环氧乙烷和一氧化碳产生丙烯酸的方法，其包括：

在羰基化反应区中使一氧化碳进料、环氧乙烷进料、CO顶部物流和BPL再循环流与羰基化催化剂和溶剂接触，且产生包括β-丙内酯、溶剂、环氧乙烷、一氧化碳、羰基化催化剂、乙醛和丁二酸酐的BPL出口流；

将所述BPL出口流的至少一部分传送到CO分离器且回收i.)所述CO顶部物流，其中所述CO顶部物流包括环氧乙烷和一氧化碳，和ii.)CO底部物流，其包括β-丙内酯、溶剂、羰基化催化剂、乙醛、丁二酸酐、环氧乙烷和一氧化碳；

将所述CO顶部物流的至少一部分传送到所述羰基化反应区；

将所述CO底部物流的至少一部分传送到羰基化催化剂再循环区的膜分离段，且将所述CO底部物流的所述至少一部分分离成i)包括保留物的BPL再循环流，所述保留物含有分离的羰基化催化剂、溶剂和β-丙内酯，和ii)包括渗透物的BPL分离流，所述渗透物含有β-丙内酯、溶剂、乙醛、丁二酸酐、环氧乙烷、一氧化碳和羰基化催化剂；

将所述BPL再循环流的至少一部分传送到所述羰基化反应区；

在包括至少一个蒸馏柱的BPL纯化区中纯化所述BPL分离流，所述至少一个蒸馏柱将所述BPL分离流进一步分离成包括溶剂的溶剂再循环流和包括β-丙内酯的纯化BPL流；

将所述纯化BPL流的至少一部分和聚合引发剂传送到具有至少一个聚合反应器的聚丙内酯反应区，所述至少一个聚合反应器使所述纯化BPL流的所述至少一部分与所述聚合引发剂接触且产生包括聚丙内酯和β-丙内酯的聚丙内酯出口流；及，

将所述聚丙内酯出口流的至少一部分传送到包括热分解反应器的丙烯酸产生区，所述热分解反应器接收所述聚丙内酯出口流的所述至少一部分且产生丙烯酸流；及，

在冷凝器中将所述丙烯酸流的至少一部分分离成(i)丙烯酸流，其包括具有至少90％纯度的丙烯酸，和(ii)有机重物质流。

24.根据权利要求23所述的方法，其中所述丙烯酸流具有纯度大于99.5％的丙烯酸且包括冰丙烯酸。

25.根据权利要求23到24中任一权利要求所述的方法，其中传送到所述丙烯酸产生区的所述聚丙内酯出口流的所述至少一部分首先传送到聚丙内酯纯化区，所述聚丙内酯纯化区包括PPL离子交换区，所述PPL离子交换区包括纯化传送到所述丙烯酸产生区的所述聚丙内酯出口流的所述至少一部分的树脂柱，使得其包括至少90wt％的聚丙内酯且移除包括阳离子羰基化催化剂物种和阴离子羰基化催化剂物种的离子物种流；且其中传送到所述丙烯酸产生区的所述聚丙内酯出口流的至少一部分在传送到所述丙烯酸产生区之前首先从所述聚丙内酯纯化区传送到聚丙内酯处理区，且所述聚丙内酯处理区将传送到所述丙烯酸产生区的所述纯化聚丙内酯出口流的所述至少一部分转化为固体形式。

26.根据权利要求23到25中任一权利要求所述的方法，其中a.)传送到所述丙烯酸产生区的所述聚丙内酯出口流的至少一部分在传送到所述丙烯酸产生区之前从所述聚丙内酯纯化区传送到PPL/BPL处理区，且所述PPL/BPL处理区具有至少一个分离区以产生i.)顶部物流，其增大传送到所述丙烯酸产生区的所述聚丙内酯出口流的所述至少一部分中的β-丙内酯的浓度，和ii.)PPL/BPL底部物流，其包括聚丙内酯，且b.)包括树脂柱的冷凝液离子交

换区接收所述有机重物质的至少一部分且将所述有机重物质分离成重物质输出流和包括阳离子羰基化催化剂物种和阴离子羰基化催化剂物种的离子物种流。

27.一种用于连续产生聚丙内酯的方法,其包括:

将β-丙内酯连续供应到第一反应器中;

将聚合引发剂连续供应到所述第一反应器中;

在所述第一反应器中产生包括聚丙内酯和未反应的β-丙内酯的第一混合物,

其中所述第一反应器包括:

β-丙内酯入口,其从β-丙内酯源接收所述β-丙内酯,

第一引发剂入口,其从引发剂源接收所述引发剂,和

第一混合物出口,其输出所述第一混合物;以及

将所述第一混合物从所述第一反应器转移到第二反应器;

任选地将其它引发剂从所述引发剂源供应到所述第二反应器;

产生包括聚丙内酯和未反应的β-丙内酯的第二混合物,

其中所述第二反应器包括:

混合物入口,其从所述第一反应器接收所述第一混合物,

任选地第二引发剂入口,其从所述引发剂源接收所述其它引发剂,和

第二混合物出口,其输出所述第二混合物。

28.一种固体可运输聚合物组合物,其包括:

至少95wt%的聚丙内酯;

小于1ppm的钴或其离子;

小于10ppm的铝或其离子;

小于10ppm乙酸;

小于500ppm的四氢呋喃;和

小于10ppm的丁二酸酐;

小于10ppm的β-丙内酯;

小于6000ppm的水。

29.一种β-丙内酯组合物,其包括:

至少99wt%的β-丙内酯;

小于10ppm的钴或其离子;

小于10ppm的铝或其离子;

小于300ppm的乙酸;

小于500ppm的丁二酸酐;

小于500ppm的四氢呋喃;

小于100ppm的环氧乙烷;

小于100ppm的乙醛;平均分子量介于800到100000g/mol之间的聚丙内酯。

用于丙烯酸及其前体的生产系统/生产方法

技术领域

[0001] 本公开大体上涉及用于利用环氧乙烷和一氧化碳生产丙烯酸及其前体的系统和方法，其前体包含β-丙内酯和聚丙内酯。

背景技术

[0002] 聚丙内酯是一种可用于许多包装和热塑性应用的可生物降解聚合物。聚丙内酯也是有用于生产丙烯酸的前体。聚丙内酯可充当冰丙烯酸的前体，生产聚丙烯酸类超吸收性聚合物、清洁联合助剂、分散剂、凝聚剂和增稠剂对聚丙内酯的需求较高。聚丙内酯的一个优势是其可以安全运输且贮存很长一段时间，而没有与装运和贮存冰丙烯酸相关的安全或品质问题。另外，对可由生物质衍生原料、石油衍生原料或其组合生产的冰丙烯酸感兴趣。鉴于丙烯酸市场的规模和丙烯酸下游应用的重要性，需要产生丙烯酸及其前体的工业系统及方法。

发明内容

[0003] 本文提供用于生产丙烯酸及其前体(包含β-丙内酯和聚丙内酯)的系统和方法，以及使用这些生产系统/生产方法的方法。在一些方面，提供利用环氧乙烷和一氧化碳用于冰丙烯酸的生产系统/生产方法以及生产方法，包含β-丙内酯生产系统/生产方法、羰基化催化剂再循环设备、β-丙内酯纯化系统、聚丙内酯生产系统/生产方法和冰丙烯酸生产系统/生产方法。

[0004] 在一些实施例中，β-丙内酯生产系统/生产方法包含一氧化碳源、环氧乙烷源、羰基化催化剂源、溶剂源和羰化反应器。在某些变化形式中，羰化反应器具有至少一个入口以从一氧化碳源接收一氧化碳，从环氧乙烷源接收环氧乙烷，从羰基化催化剂源接收羰基化催化剂，且从溶剂源接收溶剂；和一个出口以输出第一β-丙内酯流，其中第一β-丙内酯流包括β-丙内酯、溶剂、环氧乙烷、羰基化催化剂、乙醛和丁二酸酐。

[0005] 在一些实施例中，羰基化催化剂再循环设备配置成将所述催化剂的至少一部分从第一β-丙内酯流分离且产生再循环催化剂流和第二β-丙内酯流。在一些变化形式中，再循环催化剂流包含分离的羰基化催化剂。在一些变化形式中，第二β-丙内酯流包含β-丙内酯、溶剂、环氧乙烷、催化剂、乙醛和丁二酸酐。在其它实施例中，羰基化催化剂再循环设备具有：入口，从β-丙内酯生产系统/生产方法接收第一β-丙内酯流；再循环出口，将再循环催化剂流输出到羰化反应器；和β-丙内酯出口，输出第二β-丙内酯流。

[0006] 在其它实施例中，β-丙内酯纯化系统包含蒸发器、汽提器和真空柱。在一些变化形式中，蒸发器配置成从羰基化催化剂再循环设备接收第二β-丙内酯流，且将第二β-丙内酯流分离成：

[0007] 第一顶部物流，其包含(i)至少75wt％的溶剂，(ii)小于20wt％的β-丙内酯，和(iii)小于5wt％的环氧乙烷和乙醛，以及

[0008] 第一底部物流，其包含(i)至少75wt％的β-丙内酯，(ii)小于20wt％的溶剂，和

(iii)小于5wt％的催化剂、乙醛和丁二酸酐。

[0009] 在一些变化形式中，汽提器配置成从蒸发器接收第一顶部物流，且将第一顶部物流分离成：

[0010] 第二顶部物流，其包含(i)至少25wt％的环氧乙烷和乙醛，和(ii)小于75wt％的溶剂，

[0011] 侧流，其包括溶剂，和

[0012] 第二底部物流，其包括β-丙内酯。

[0013] 在一些变化形式中，真空柱配置成从蒸发器接收第一底部物流，且从汽提器接收第二底部物流，且将第一底部物流与第二底部物流混合以产生混合底部物流，将第一底部物流和第二底部物流分离成包括溶剂的第三顶部物流和包括β-丙内酯的第三底部物流。

[0014] 在一些实施例中，聚丙内酯生产系统/生产方法包含：

[0015] 聚合引发剂或催化剂源；

[0016] 至少一个聚合反应器，其从β-丙内酯纯化系统接收第三底部物流且从聚合引发剂或催化剂源接收聚合引发剂或催化剂，且输出聚丙内酯流，其中聚丙内酯流包括聚丙内酯和β-丙内酯。

[0017] 在其它实施例中，冰丙烯酸生产系统/生产方法包含热分解反应器，所述热分解反应器具有：入口，其从聚丙内酯生产系统/生产方法接收聚丙内酯流；和出口，其输出冰丙烯酸流，其中冰丙烯酸流包括冰丙烯酸。

[0018] 在其它方面，提供聚丙内酯生产系统/生产方法，其包含：β-丙内酯源；聚合引发剂或催化剂源；第一聚合反应器；和第二聚合反应器。

[0019] 在一些变化形式中，第一聚合反应器包含：β-丙内酯入口，其从β-丙内酯源接收β-丙内酯；第一催化剂入口，其从聚合催化剂源接收催化剂；和第一混合物出口，其输出第一混合物。在一种变化形式中，第一混合物包括聚丙内酯、β-丙内酯和聚合催化剂。

[0020] 在其它变化形式中，第二聚合反应器在第一聚合反应器之后放置，且包含：混合物入口，其从第一聚合反应器接收第一混合物；第二催化剂入口，其从羰基化催化剂源接收其它聚合催化剂；和第二混合物出口，其输出第二混合物。在一种变化形式中，第二混合物包括聚丙内酯、β-丙内酯和聚合催化剂。

[0021] 在某些方面，提供β-丙内酯聚合剂，其包含：混合区，其配置成混合β-丙内酯与催化剂；和多个冷却区，其在混合区之后放置。在一些变化形式中，β-丙内酯聚合剂具有反应长度。在某些变化形式中，在引发剂或催化剂存在下至多95％的β-丙内酯聚合以在反应长度的第一个25％中形成聚丙内酯。

[0022] 在其它方面，提供一种用于连续生产聚丙内酯的方法，其包含：

[0023] 将β-丙内酯连续供应到第一反应器中；

[0024] 将催化剂连续供应到第一反应器中；

[0025] 在第一反应器中产生包括聚丙内酯、未反应的β-丙内酯和残余催化剂的第一混合物，

[0026] 将第一混合物从第一反应器转移到第二反应器；

[0027] 将其它催化剂从所述催化剂源供应到第二反应器；

[0028] 在第二反应器中产生包括聚丙内酯、未反应的β-丙内酯和残余催化剂的第二混合

物。

[0029] 在方法的一些变化形式中，第一反应器具有：β-丙内酯入口，其从β-丙内酯源接收β-丙内酯；第一催化剂入口，其从催化剂源接收催化剂；和第一混合物出口，其输出第一混合物。在方法的其它变化形式中，第二反应器具有：混合物入口，其从第一反应器接收第一混合物；第二催化剂入口，其从催化剂源接收其它催化剂；和第二混合物出口，其输出第二混合物。

[0030] 在其它方面中，提供一种聚丙内酯生产系统/生产方法，其包含：β-丙内酯源；第一反应器；和第二反应器。在一些实施例中，第一反应器具有：β-丙内酯入口，其从β-丙内酯源接收β-丙内酯；载体催化剂或载体催化剂前体的床；和第一混合物出口，其输出第一混合物。在一种变化形式中，第一混合物包括聚丙内酯和未反应的β-丙内酯。在其它实施例中，第二反应器在第一反应器之后放置。在一些变化形式中，混合物入口配置成从第一反应器、载体催化剂或载体催化剂前体的第二床接收第一混合物，且第二混合物出口配置成输出第二混合物。在一种变化形式中，第二混合物包括聚丙内酯和未反应的β-丙内酯。

[0031] 在其它方面中，提供固体可运输聚合物组合物，其包含：至少95wt％的β-丙内酯；小于10ppm的钴或其离子；小于10ppm的铝或其离子；小于10ppm的乙酸；和小于10ppm的四氢呋喃。

[0032] 在另一方面中，提供β-丙内酯纯化系统，其包含：蒸发器、第一柱和第二柱。在一些实施例中，蒸发器配置成接收进料流，其中进料流包括β-丙内酯、溶剂，且将进料流分离成：第一顶部物流，其包括：(i)至少75wt％的溶剂和(ii)至多20wt％的β-丙内酯；以及第一底部物流，其包括：(i)至少75wt％的β-丙内酯，和(ii)至多20wt％的溶剂。

[0033] 在一些变化形式中，第一柱配置成从蒸发器接收第一顶部物流，且将第一顶部物流分离成：第二顶部物流，其包括：(i)至少35wt％的环氧乙烷，和(ii)至多60wt％的溶剂；侧流，其包括溶剂；和第二底部物流，其包括至少75wt％的β-丙内酯。

[0034] 在其它变化形式中，第二柱配置成从蒸发器接收第一底部物流，且从第一柱接收第二底部物流，并且将第一底部物流和第二底部物流分离成：第三顶部物流，其包括至少95wt％的溶剂；和第三底部物流，其包括至少95wt％的β-丙内酯。

[0035] 在一个方面中，提供一种β-丙内酯组合物，其包含至少95wt％的β-丙内酯；小于10ppm的钴或其离子；小于10ppm的铝或其离子；小于10ppm的乙酸；和小于10ppm的四氢呋喃。

[0036] 在其它方面中，提供一种β-丙内酯生产系统/生产方法，其包含：一氧化碳源；环氧乙烷源；羰基化催化剂源；溶剂源；再循环溶剂存储罐；反应器；和纯化设备。在一些实施例中，反应器具有：至少一个入口，其从一氧化碳源接收一氧化碳，从环氧乙烷源接收环氧乙烷，从羰基化催化剂源接收羰基化催化剂，且从溶剂源和再循环溶剂存储罐接收溶剂；和出口，其输出混合物，其中混合物包括β-丙内酯、溶剂、未反应的一氧化碳、未反应的环氧乙烷和羰基化催化剂。在其它实施例中，纯化设备配置成：从混合物分离溶剂，且将分离的溶剂转移到再循环溶剂储液器。

[0037] 在一个方面中，提供一种冰丙烯酸生产系统/生产方法，其包含：聚丙内酯源；和反应器。在一些实施例中，聚丙内酯源包含：至少95wt％的聚丙内酯；小于10ppm的钴或其离子；小于10ppm的铝或其离子；小于10ppm的乙酸；和小于10ppm的四氢呋喃。在其它实施例

中，反应器具有：入口，其配置成从聚丙内酯源接收聚丙内酯；和出口，其配置成输出混合物，其中混合物包括冰丙烯酸。

[0038] 在其它方面中，提供一种分离系统，其包含：进料源；膜；第一泵；和第二泵。在一些实施例中，所述膜具有：入口，其从进料源接收进料流，其中进料流包括β-丙内酯、催化剂和溶剂；催化剂出口，其输出包括催化剂和溶剂的催化剂再循环流；和β-丙内酯出口，其输出包括β-丙内酯和溶剂的β-丙内酯流。在其它实施例中，第一泵配置成将进料流从进料源泵送到膜。在其它实施例中，第二泵配置成将催化剂再循环流泵送到β-丙内酯生产系统/生产方法。

附图说明

[0039] 可参考结合附图获取的以下描述最佳地理解本发明，其中类似部件可以由类似编号指代。

[0040] 图1是利用一氧化碳和环氧乙烷生产丙烯酸的系统的示意性说明。

[0041] 图2是利用β-丙内酯生产聚丙内酯且利用聚丙内酯生产冰丙烯酸的单元操作的示意性说明。

[0042] 图3是采用膜的羰基化催化剂再循环系统的示意性说明，所述膜配置成从β-丙内酯产物流分离残余羰基化催化剂。

[0043] 图4A是用于将β-丙内酯转化为聚丙内酯的系统的示意性说明，所述系统涉及使用两个串联的连续搅拌罐反应器。

[0044] 图4B是用于将β-丙内酯转化为聚丙内酯的系统的示意性说明，所述系统涉及使用两个串联的环管反应器。

[0045] 图5是用于将β-丙内酯转化为聚丙内酯的系统的示意性说明，所述系统涉及具有多个冷却区的推流式反应器。

[0046] 图6到13描绘利用环氧乙烷和一氧化碳通过生产β-丙内酯和聚丙内酯来生产冰丙烯酸的生产系统/生产方法的各种配置。

[0047] 图14说明本文中所描述的丙烯酸生产系统/生产方法的一实施例。

[0048] 图15说明本文中所描述的羰基化反应系统的一实施例。

[0049] 图16说明本文中所描述的BPL纯化系统的一实施例。

[0050] 图17到20是与实例1相关的标绘图且示出PPL和bPL峰吸光度随时间变化的标绘图；分离的固体的^{1}H NMR；分离的固体的TGA；和120℃下分离的固体的熔体流变性数据。

[0051] 图21到24是与实例2相关的标绘图且示出PPL和bPL峰吸光度随时间变化的标绘图；分离的固体的^{1}H NMR；分离的固体的TGA；和120℃下分离的固体的熔体流变性数据。

[0052] 图25到28是与实例4相关的标绘图且示出指示丙烯酸的回收的^{1}H NMR标绘图。

[0053] 图29是与实例5相关的标绘图且示出指示丙烯酸的回收的^{1}H NMR标绘图。

具体实施方式

[0054] 以下描述阐述示范性方法、参数等。然而，应认识到，此类描述不打算作为对本揭示的范围的限制，而是打算提供为示范性实施例的描述。

[0055] 定义

[0056] 下文更详细描述特定官能团和化学术语的定义。化学元素是根据元素周期表(the Periodic Table of the Elements),CAS版本,化学和物理学手册(Handbook of Chemistry and Physics),第75版,封里来识别,并且特定官能团大体上如其中所描述定义。另外,有机化学的一般原理以及特定官能性部分和反应性描述于《有机化学(Organic Chemistry)》,Thomas Sorrell,大学科学书籍(University Science Books),索萨利托(Sausalito),1999;Smith和March,《马奇高等有机化学(March's Advanced Organic Chemistry)》,第5版,约翰·威利父子公司(John Wiley&Sons,Inc.),纽约(New York),2001;Larock,《综合有机转化(Comprehensive Organic Transformations)》,VCH出版公司(VCH Publishers,Inc.),纽约,1989;Carruthers,《一些现代有机合成方法(Some Modern Methods of Organic Synthesis)》,第3版,剑桥大学出版社(Cambridge University Press),剑桥(Cambridge),1987中;其中每一者的全部内容以引用的方式并入本文中。

[0057] 如本文所用,术语"卤基"和"卤素"是指选自氟(氟基,-F)、氯(氯基,-Cl)、溴(溴基,-Br)以及碘(碘基,-I)的原子。

[0058] 如本文所用,术语"脂肪族"或"脂肪族基团"表示可以是直链(即非支链)、支链或环状(包含稠合、桥接和螺稠合多环),并且可以是完全饱和或可含有一或多个不饱和单元,但不是芳香族的烃部分。除非另外说明,否则脂肪族基团含有1到30个碳原子。在一些实施例中,脂肪族基团含有1到12个碳原子。在一些实施例中,脂肪族基团含有1到8个碳原子。在一些实施例中,脂族基含有1到6个碳原子。在一些实施例中,脂肪族基团含有1到5个碳原子,在一些实施例中,脂肪族基团含有1到4个碳原子,在另外其它实施例中,脂肪族基团含有1到3个碳原子,并且在另外其它实施例中,脂肪族基团含有1到2个碳原子。合适的脂肪族基团包含但不限于直链或支链烷基、烯基以及炔基,和其混杂,如(环烷基)烷基、(环烯基)烷基或(环烷基)烯基。

[0059] 如本文所用,术语"杂脂肪族"是指其中一或多个碳原子独立地经一或多个选自由以下组成的群组的原子置换的脂肪族基团:氧、硫、氮、磷或硼。在一些实施例中,一个或两个碳原子独立地经氧、硫、氮或磷中的一或多个置换。杂脂肪族基团可以是经取代或未经取代、支链或非支链、环状或非环状的,并且包含"杂环(heterocycle)"、"杂环基"、"杂环脂肪族"或"杂环(heterocyclic)"基团。

[0060] 如本文所用,术语"丙烯酸酯(acrylate/acrylates)"是指任何具有与酰基羰基相邻的乙烯基的酰基。所述术语涵盖经单取代、二取代和三取代的乙烯基。丙烯酸酯的实例包含但不限于:丙烯酸酯、甲基丙烯酸酯、乙基丙烯酸酯、肉桂酸酯(3-苯基丙烯酸酯)、巴豆酸酯、惕各酸酯(tiglate)以及异戊烯酸酯。

[0061] 如本文所用,术语"聚合物"是指具有高相对分子量的分子,其结构包括实际上或概念上来源于具有低相对分子量的分子的单元的多重重复。在一些实施例中,聚合物仅由一种单体物种(例如聚氧化乙烯)构成。在一些实施例中,聚合物为一或多种环氧化物的共聚物、三元共聚物、杂聚物、嵌段共聚物或递变杂聚物。

[0062] 如本文所用,术语"不饱和"意味着部分具有一或多个双键或三键。

[0063] 单独或作为较大部分的一部分使用的术语"环脂肪族"、"碳环(carbocycle)"或"碳环(carbocyclic)"是指如本文所描述,具有3到12个成员的饱和或部分不饱和环状脂肪族单环、双环或多环系统,其中脂肪族环系统如上文所定义和本文中所描述任选地经取代。

环脂肪族基团包含但不限于环丙基、环丁基、环戊基、环戊烯基、环己基、环己烯基、环庚基、环庚烯基、环辛基、环辛烯基以及环辛二烯基。在一些实施例中，环烷基具有3到6个碳原子。术语“环脂肪族”、“碳环(carbocycle)”或“碳环(carbocyclic)”还包含与一或多个芳香族或非芳香族环稠合的脂肪族环，例如十氢萘基或四氢萘基，其中连接基团或连接点位于脂肪族环上。在一些实施例中，碳环基是双环的。在一些实施例中，碳环基是三环的。在一些实施例中，碳环基是多环的。

[0064] 如本文所用，术语“烷基”是指通过移除单个氢原子而从含有介于一与六个之间的碳原子的脂肪族部分获得的饱和、直链或支链烃基。除非另外说明，否则烷基含有1到12个碳原子。在一些实施例中，烷基含有1到8个碳原子。在一些实施例中，烷基含有1到6个碳原子。在一些实施例中，烷基含有1到5个碳原子，在一些实施例中，烷基含有1到4个碳原子，在另外其它实施例中，烷基含有1到3个碳原子，且在另外其它实施例中，烷基含有1到2个碳原子。烷基的实例包含但不限于甲基、乙基、正丙基、异丙基、正丁基、异丁基、仲丁基、仲戊基、异戊基、叔丁基、正戊基、新戊基、正己基、仲己基、正庚基、正辛基、正癸基、正十一烷基、十二烷基等。

[0065] 如本文所用，术语“烯基”表示通过移除单个氢原子而从具有至少一个碳-碳双键的直链或支链脂肪族部分获得的单价基团。除非另外说明，否则烯基含有2到12个碳原子。在一些实施例中，烯基含有2到8个碳原子。在一些实施例中，烯基含有2到6个碳原子。在一些实施例中，烯基含有2到5个碳原子，在一些实施例中，烯基含有2到4个碳原子，在另外其它实施例中，烯基含有2到3个碳原子，且在另外其它实施例中，烯基含有2个碳原子。烯基包含例如乙烯基、丙烯基、丁烯基、1-甲基-2-丁烯-1-基等。

[0066] 如本文所用，术语“炔基”是指通过移除单个氢原子而从具有至少一个碳-碳三键的直链或支链脂肪族部分获得的单价基团。除非另外说明，否则炔基含有2到12个碳原子。在一些实施例中，炔基含有2到8个碳原子。在一些实施例中，炔基含有2到6个碳原子。在一些实施例中，炔基含有2到5个碳原子，在一些实施例中，炔基含有2到4个碳原子，在另外其它实施例中，炔基含有2到3个碳原子，且在另外其它实施例中，炔基含有2个碳原子。代表性炔基包含但不限于乙炔基、2-丙炔基(炔丙基)、1-丙炔基等。

[0067] 如本文所用，术语“碳环(carbocycle/carbocyclic ring)”是指环仅含有碳原子的单环和多环部分。除非另外说明，否则碳环可以是饱和、部分不饱和或芳香族的，并且含有3到20个碳原子。代表性碳环包含环丙烷、环丁烷、环戊烷、环己烷、双环[2,2,1]庚烷、降冰片烯、苯基、环己烯、萘以及螺环[4.5]癸烷。

[0068] 单独或作为较大部分的一部分使用的术语“芳基”，如在“芳烷基”、“芳烷氧基”或“芳氧基烷基”中，是指具有总共5到20个环成员的单环和多环系统，其中系统中的至少一个环是芳香族的并且其中系统中的各环含有三到十二个环成员。术语“芳基”可与术语“芳基环”互换使用。在一些实施例中，“芳基”是指包含但不限于苯基、萘基、蒽基等的芳香族环系统，其可以带有一或多个取代基。如本文所用，在术语“芳基”范围内也包含芳香族环稠合到一或多个额外环的基团，例如苯并呋喃基、二氢茚基、邻苯二甲酰亚胺基、萘酰亚胺基、啡啶基或四氢萘基等。

[0069] 单独或作为较大部分的一部分使用的术语“杂芳基”和“杂芳-”，例如“杂芳烷基”或“杂芳烷氧基”是指具有5到14个环原子，优选地5、6、9或10个环原子；具有在环阵列中共

用的6、10或14个π电子;和除碳原子以外具有一到五个杂原子的基团。术语“杂原子”是指氮、氧或硫,并且包含氮或硫的任何氧化形式以及碱性氮的任何季铵化形式。杂芳基包括(但不限于)噻吩基、呋喃基、吡咯基、咪唑基、吡唑基、三唑基、四唑基、噁唑基、异噁唑基、噁二唑基、噻唑基、异噻唑基、噻二唑基、吡啶基、哒嗪基、嘧啶基、吡嗪基、吲哚嗪基、嘌呤基、萘啶基、苯并呋喃基以及喋啶基。如本文所用,术语“杂芳基”和“杂芳-”还包含杂芳香族环与一或多个芳基、环脂肪族或杂环基环稠合的基团,其中连接基团或连接点位于杂芳香族环上。非限制性实例包含吲哚基、异吲哚基、苯并噻吩基、苯并呋喃基、二苯并呋喃基、吲唑基、苯并咪唑基、苯并噻唑基、喹啉基、异喹啉基、噌啉基、酞嗪基、喹唑啉基、喹喔啉基、4H-喹嗪基、咔唑基、吖啶基、啡嗪基、啡噻嗪基、啡噁嗪基、四氢喹啉基、四氢异喹啉基以及吡啶并[2,3-b]-1,4-噁嗪-3(4H)-酮。杂芳基可以是单环或双环的。术语“杂芳基(heteroaryl)”与术语“杂芳基环(heteroaryl ring)”、“杂芳基(heteroaryl group)”或“杂芳族(heteroaromatic)”可互换使用,这些术语中的任一个都包含任选地经取代的环。术语“杂芳烷基”是指经杂芳基取代的烷基,其中烷基和杂芳基部分独立地任选地经取代。

[0070] 如本文所用,术语“杂环(heterocycle)”、“杂环基(heterocyclyl)”、“杂环基(heterocyclic radical)”和“杂环(heterocyclic ring)”可互换使用并且是指稳定5到7元单环或7到14元双环杂环部分,其是饱和或部分不饱和的,并且除碳原子以外具有一或多个、优选地一到四个如上文所定义的杂原子。当关于杂环的环原子使用时,术语“氮”包含经取代的氮。作为一实例,在具有0到3个选自氧、硫或氮的杂原子的饱和或部分不饱和环中,氮可以是N(如在3,4-二氢-2H-吡咯基中)、NH(如在吡咯烷基中)或$^{+}$NR(如在N-经取代吡咯烷基中)。

[0071] 杂环可以在任何杂原子或碳原子处连接到其侧基,从而产生稳定结构,并且任何环原子可以任选地经取代。此类饱和或部分不饱和杂环基团的实例包含但不限于四氢呋喃基、四氢噻吩基、吡咯烷基、吡咯烷酮基、哌啶基、吡咯啉基、四氢喹啉基、四氢异喹啉基、十氢喹啉基、噁唑烷基、哌嗪基、二氧杂环己烷基、二氧戊环基、二氮杂卓基、氧氮杂环庚烷基、硫氮杂卓基、吗啉基以及奎宁环基。术语“杂环(heterocycle)”、“杂环基(heterocyclyl)”、“杂环基环(heterocyclyl ring)”、“杂环基(heterocyclic group)”、“杂环部分(heterocyclic moiety)”和“杂环基(heterocyclic radical)”在本文中可互换使用,并且还包含杂环基环稠合到一或多个芳基、杂芳基或环脂肪族环的基团,例如吲哚啉基、3H-吲哚基、色满基、啡啶基或四氢喹啉基,其中连接基团或连接点位于杂环基环上。杂环基可以是单环或双环的。术语“杂环基烷基”是指经杂环基取代的烷基,其中烷基和杂环基部分独立地任选地经取代。

[0072] 如本文所用,术语“部分不饱和”是指包含至少一个双键或三键的环部分。如本文所定义,术语“部分不饱和”打算涵盖具有多个不饱和位置的环,但并不打算包含芳基或杂芳基部分。

[0073] 如本文中所描述,化合物可含有“任选地经取代”部分。一般来说,术语“经取代”无论前面有还是没有术语“任选地”,都意指指定部分的一个或多个氢经适合的取代基置换。除非另外指示,否则“任选地经取代”基团可以在基团的每个可取代位置处具有合适的取代基,并且当任何既定结构中的一个以上位置可以经一个以上选自规定基团的取代基取代时,在每一位置处取代基可以是相同或不同的。所设想的取代基的组合可包含促使形成稳

定或化学上可行的化合物的那些组合。如本文所用，出于揭示于本文中的目的中的一或多个，术语「稳定」是指在经受以下条件时不实质上改变的化合物：允许其生产、检测，以及在一些实施例中，允许其回收、纯化和使用。

[0074] 在本文中的一些化学结构中，取代基显示为连接到与所描绘分子的环中的键交叉的键。这意味着取代基中的一或多个可以在任何可用的位置连接到环(通常置换母体结构的氢原子)。在如此经取代的环的原子具有两个可取代位置的情况下，两个基团可以存在于同一个环原子上。当存在多于一个取代基时，各自独立于其它取代基定义，并且各自可以具有不同结构。在显示与环的键交叉的取代基是-R的情况下，此具有如同环如先前段落中所描述称为“任选地经取代”相同的含义。

[0075] “任选地经取代”基团的可取代碳原子上合适的单价取代基独立地为卤素；$-(CH_2)_{0-4}R^{\circ}$；$-(CH_2)_{0-4}OR^{\circ}$；$-O-(CH_2)_{0-4}C(O)OR^{\circ}$；$-(CH_2)_{0-4}CH(OR^{\circ})_2$；$-(CH_2)_{0-4}SR^{\circ}$；$-(CH_2)_{0-4}Ph$，其可以经$R^{\circ}$取代；$-(CH_2)_{0-4}O(CH_2)_{0-1}Ph$，其可以经$R^{\circ}$取代；-CH=CHPh，其可以经$R^{\circ}$取代；$-NO_2$；-CN；$-N_3$；$-(CH_2)_{0-4}N(R^{\circ})_2$；$-(CH_2)_{0-4}N(R^{\circ})C(O)R^{\circ}$；$-N(R^{\circ})C(S)R^{\circ}$；$-(CH_2)_{0-4}N(R^{\circ})C(O)NR^{\circ}_2$；$-N(R^{\circ})C(S)NR^{\circ}_2$；$-(CH_2)_{0-4}N(R^{\circ})C(O)OR^{\circ}$；$-N(R^{\circ})N(R^{\circ})C(O)R^{\circ}$；$-N(R^{\circ})N(R^{\circ})C(O)NR^{\circ}_2$；$-N(R^{\circ})N(R^{\circ})C(O)OR^{\circ}$；$-(CH_2)_{0-4}C(O)R^{\circ}$；$-C(S)R^{\circ}$；$-(CH_2)_{0-4}C(O)OR^{\circ}$；$-(CH_2)_{0-4}C(O)N(R^{\circ})_2$；$-(CH_2)_{0-4}C(O)SR^{\circ}$；$-(CH_2)_{0-4}C(O)OSiR^{\circ}_3$；$-(CH_2)_{0-4}OC(O)R^{\circ}$；$-OC(O)(CH_2)_{0-4}SR^{\circ}$；$-SC(S)SR^{\circ}$；$-(CH_2)_{0-4}SC(O)R^{\circ}$；$-(CH_2)_{0-4}C(O)NR^{\circ}_2$；$-C(S)NR^{\circ}_2$；$-C(S)SR^{\circ}$；$-SC(S)SR^{\circ}$；$-(CH_2)_{0-4}OC(O)NR^{\circ}_2$；$-C(O)N(OR^{\circ})R^{\circ}$；$-C(O)C(O)R^{\circ}$；$-C(O)CH_2C(O)R^{\circ}$；$-C(NOR^{\circ})R^{\circ}$；$-(CH_2)_{0-4}SSR^{\circ}$；$-(CH_2)_{0-4}S(O)_2R^{\circ}$；$-(CH_2)_{0-4}S(O)_2OR^{\circ}$；$-(CH_2)_{0-4}OS(O)_2R^{\circ}$；$-S(O)_2NR^{\circ}_2$；$-(CH_2)_{0-4}S(O)R^{\circ}$；$-N(R^{\circ})S(O)_2NR^{\circ}_2$；$-N(R^{\circ})S(O)_2R^{\circ}$；$-N(OR^{\circ})R^{\circ}$；$-C(NH)NR^{\circ}_2$；$-P(O)_2R^{\circ}$；$-P(O)R^{\circ}_2$；$-OP(O)R^{\circ}_2$；$-OP(O)(OR^{\circ})_2$；$SiR^{\circ}_3$；$-(C_{1-4}$直链或支链亚烷基$)O-N(R^{\circ})_2$；或$-(C_{1-4}$直链或支链亚烷基$)C(O)O-N(R^{\circ})_2$，其中每个$R^{\circ}$可以如下文所定义经取代，并且独立地为氢、$C_{1-8}$脂肪族、$-CH_2Ph$、$-O(CH_2)_{0-1}Ph$，或具有0到4个独立地选自氮、氧和硫的杂原子的5到6元饱和、部分不饱和或芳基环，或尽管如上定义，但两个独立出现的R°与其中间原子结合在一起形成具有0到4个独立地选自氮、氧和硫的杂原子的3到12元饱和、部分不饱和或芳基单环或多环，其可以如下文所定义经取代。

[0076] R°上合适的单价取代基(或通过连同其中间原子一起获取两个独立存在的R°来形成的环)独立地为卤素、$-(CH_2)_{0-2}R^{\bullet}$、$-($卤基$R^{\bullet})$、$-(CH_2)_{0-2}OH$、$-(CH_2)_{0-2}OR^{\bullet}$、$-(CH_2)_{0-2}CH(OR^{\bullet})_2$、$-O($卤基$R^{\bullet})$、-CN、$-N_3$、$-(CH_2)_{0-2}C(O)R^{\bullet}$、$-(CH_2)_{0-2}C(O)OH$、$-(CH_2)_{0-2}C(O)OR^{\bullet}$、$-(CH_2)_{0-4}C(O)N(R^{\circ})_2$、$-(CH_2)_{0-2}SR^{\bullet}$、$-(CH_2)_{0-2}SH$、$-(CH_2)_{0-2}NH_2$、$-(CH_2)_{0-2}NHR^{\bullet}$、$-(CH_2)_{0-2}NR^{\bullet}_2$、$-NO_2$、$-SiR^{\bullet}_3$、$-OSiR^{\bullet}_3$、$-C(O)SR^{\bullet}$、$-(C_{1-4}$直链或支链亚烷基$)C(O)OR^{\bullet}$或$-SSR^{\bullet}$，其中每个$R^{\bullet}$未经取代或当前面有“卤基”时仅经一或多个卤素取代，并且独立地选自C_{1-4}脂肪族、$-CH_2Ph$、$-O(CH_2)_{0-1}Ph$或具有0到4个独立地选自氮、氧和硫的杂原子的5到6元饱和、部分不饱和或芳基环。R°的饱和碳原子上合适的二价取代基包含=O和=S。

[0077] “任选地经取代”基团的饱和碳原子上合适的二价取代基包含以下：=O、=S、$=NNR^*_2$、$=NNHC(O)R^*$、$=NNHC(O)OR^*$、$=NNHS(O)_2R^*$、$=NR^*$、$=NOR^*$、$-O(C(R^*_2))_{2-3}O-$或$-S(C(R^*_2))_{2-3}S-$，其中每个独立出现的R*选自氢、可以如下文所定义经取代的C_{1-6}脂肪族或具有0到4个独立地选自氮、氧和硫的杂原子的未经取代5到6元饱和、部分不饱和或芳基环。结合到“任选经取代”基团的邻接可取代碳的适合的二价取代基包含：$-O(CR^*_2)_{2-3}O-$，其中每个独

立出现的R*选自氢、可以如下文所定义经取代的C_{1-6}脂肪族基团或具有0到4个独立地选自氮、氧和硫的杂原子的未经取代5到6元饱和、部分不饱和或芳基环。

[0078] R*的脂肪族基团上合适的取代基包含卤素、-R●、-(卤基R●)、-OH、-OR●、-O(卤基R●)、-CN、-C(O)OH、-C(O)OR●、$-NH_2$、-NHR●、$-NR●_2$或$-NO_2$,其中每个R●未经取代或当前面有"卤基"时仅经一或多个卤素取代,并且独立地为C_{1-4}脂肪族、$-CH_2Ph$、$-O(CH_2)_{0-1}Ph$或具有0到4个独立地选自氮、氧和硫的杂原子的5到6元饱和、部分不饱和或芳基环。

[0079] "任选地经取代"基团的可取代氮上合适的取代基包含$-R^{\dagger}$、$-NR^{\dagger}_2$、$-C(O)R^{\dagger}$、$-C(O)OR^{\dagger}$、$-C(O)C(O)R^{\dagger}$、$-C(O)CH_2C(O)R^{\dagger}$、$-S(O)_2R^{\dagger}$、$-S(O)_2NR^{\dagger}_2$、$-C(S)NR^{\dagger}_2$、$-C(NH)NR^{\dagger}_2$或$-N(R^{\dagger})S(O)_2R^{\dagger}$,其中每个$R^{\dagger}$独立地为氢、可以如下文所定义经取代的$C_{1-6}$脂肪族、未经取代-OPh或具有0到4个独立地选自氮、氧和硫的杂原子的未经取代5到6元饱和、部分不饱和或芳基环,或尽管如上定义,但两个独立存在的$R^{\dagger}$与其中间原子结合在一起形成具有0到4个独立地选自氮、氧和硫的杂原子的未经取代3到12元饱和、部分不饱和或芳基单环或双环。

[0080] $R^{\dagger}$的脂肪族基团上合适的取代基独立地为卤素、-R●、-(卤基R●)、-OH、-OR●、-O(卤基R●)、-CN、-C(O)OH、-C(O)OR●、$-NH_2$、-NHR●、$-NR●_2$或$-NO_2$,其中每个R●未经取代或当前面有"卤基"时仅经一或多个卤素取代,并且独立地为C_{1-4}脂肪族、$-CH_2Ph$、$-O(CH_2)_{0-1}Ph$或具有0到4个独立地选自氮、氧和硫的杂原子的5到6元饱和、部分不饱和或芳基环。

[0081] 如本文所用,术语"催化剂"是指一种物质,其在存在时可增加化学反应的速率,而其自身不会消耗或发生永久性化学变化。

[0082] 如本文所用,一或多个数值前面的术语"约"意指所述数值±5%。应理解,本文中提及"约"值或参数包含(且描述)针对所述值或参数本身的实施例。举例来说,提到"约x"的描述包含"x"本身的描述。

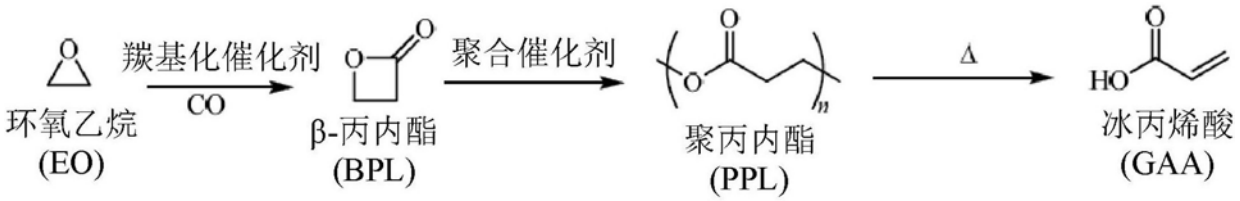
[0083] 另外,应理解,本文中提及两个值或参数"之间"包含(且描述)包含所述两个值或参数本身的实施例。举例来说,提到"介于x与y之间"的描述包含"x"和"y"本身的描述。

[0084] 本文中所揭示的质量分数可通过乘以100来转换成wt%。

[0085] 冰丙烯酸生产系统/生产方法

[0086] 冰丙烯酸可由环氧乙烷和一氧化碳根据以下通用反应流程生产:

[0087]



[0088] 环氧乙烷("EO")可以在羰基化催化剂存在下例如与一氧化碳("CO")发生羰基化反应以产生β-丙内酯("bPL")。β-丙内酯可以在聚合催化剂存在下进行聚合以产生聚丙内酯("PPL")。聚丙内酯可以进行热分解以产生冰丙烯酸("GAA")。

[0089] PPL可以通过如由(岩渕(Iwabuchi),S.,哈克斯(Jaacks),V.,加利尔(Galil),F.和克恩(Kern),W.(1973),聚(氧羰基乙烯)(聚-β-丙内酯)的热降解(The thermal degradation of poly(oxycarbonylethylene)(poly-β-propiolactone)).《大分子化学

(Makromol.Chem.)》,165:59-72)所揭示的两个主要反应机理中的一个来进行热分解。所需机理被称作解链,并且其将具有链长为“n”的PPL聚合物转化成丙烯酸的一个分子并将PPL聚合物链长减短到n-1。另一方法被称作链断裂;链断裂将链长为n的PPL聚合物转化成链长小于n-2的PPL聚合物和链长至少为2的PPL聚合物。

[0090] 产物丙烯酸通过两种机理,迈克尔加成(Michael addition)或自由基聚合,容易发生自动聚合。迈克尔加成形成两个丙烯酸分子的产物,其是二丙烯酸酯并且与链长为2的PPL一致。不存在已知的丙烯酸迈克尔加成抑制剂,但在热分解条件下,此反应是可逆的并且可以分解回两个丙烯酸分子。丙烯酸的自由基聚合产物产生聚丙烯酸,且在热分解条件下通常不会转化回丙烯酸。存在许多已知的丙烯酸自由基聚合抑制剂,包含但不限于啡噻嗪(PTZ)和4-甲氧基苯酚(MEHQ)。在许多情形下,自由基聚合抑制剂流(无溶剂或在适当溶剂中)以间歇或连续模式添加到主要热分解反应器,或在引入到反应器之前与PPL流混合,以在热分解反应器中对抗丙烯酸到聚丙烯酸的损耗。

[0091] PPL的热分解可以利用解聚催化剂的存在来催化。解聚催化剂(无溶剂或在适当溶剂中)可以间歇或连续模式添加到主要热分解反应器,或在引入到反应器之前与PPL流混合,以减小热分解反应条件的强度(其减少丙烯酸到聚丙烯酸的转化)。最佳地,所采用的bPL聚合催化剂也可用作解聚催化剂。热分解反应器可经设计(参见下文)以使得PPL入口流和热分解反应器中的聚合催化剂物种的浓度连同反应器条件和流组成的差别说明表面上相异的作用。

[0092] 本文提供用于按工业规模利用环氧乙烷和一氧化碳生产冰丙烯酸的系统和方法。举例来说,在一些方面中,本文中所描述的系统和方法适合于按25千吨每年(“KTA”)的规模生产冰丙烯酸。在一些变化形式中,本文所提供的系统被配置成以连续方法产生冰丙烯酸,并且进一步反馈回路以连续产生丙烯酸。

[0093] 另外,在一些变化形式中,本文所提供的系统进一步包含各种纯化系统以产生高纯度的冰丙烯酸。举例来说,本文所提供的系统可以被配置成移除残余羰基化催化剂、羰基化溶剂和副产物(例如乙醛、丁二酸酐和丙烯酸二聚体)以获得纯度为至少99.5%、至少99.6%、至少99.7%、至少99.8%或至少99.9%的冰丙烯酸。

[0094] 在其它变化形式中,本文所提供的系统还被配置成再循环各种起始材料和冰丙烯酸前体,例如聚丙内酯。举例来说,系统可包含一或多个再循环系统以隔离未反应的环氧乙烷、未反应的一氧化碳、羰基化溶剂和催化剂。

[0095] 在其它变化形式中,本文所提供的系统还被配置成管理和集成所产生的热。产生β-丙内酯的羰基化反应和产生聚丙内酯的聚合反应是放热的。因此,由放热单元操作,例如羰基化反应器和聚合反应器产生的热可采集并且在吸热单元操作,例如蒸馏设备和热分解反应器中用于冷却。举例来说,在本文所提供的系统和方法的一些变化形式中,蒸汽可以利用过程流体与水/蒸汽之间的温度梯度在传热设备(例如壳管式热交换器和反应器冷却夹套)中产生。此蒸汽可用于在放热与吸热单元操作之间热集成。在本文所提供的系统和方法的其它变化形式中,可使用其它合适的传热流体。

[0096] 在其它变化形式中,热集成可以通过组合某些单元操作来实现。举例来说,热集成可以通过在单个单元操作内组合β-丙内酯聚合与来自蒸馏柱的溶剂(例如THF)蒸发来实现。在此类配置中,从β-丙内酯聚合反应释放的热直接用于蒸发蒸馏设备中的溶剂,并且单

元的输出产生聚丙内酯。在其它变化形式中，从聚合反应释放的热可导出到同一生产场所的其它系统。

[0097] 参考图1，描绘了一种利用一氧化碳和环氧乙烷产生丙烯酸的示范性系统。将一氧化碳(CO)、羰基化催化剂、环氧乙烷(EO)和羰基化溶剂供应到图1中描绘为连续搅拌罐反应器(CSTR)的β-丙内酯生产系统/生产方法中。此类β-丙内酯生产系统/生产方法通常被配置成产生β-丙内酯的液体产物流。将此β-丙内酯产物流供应到图1中描绘为闪蒸罐的EO/CO分离器，其中未反应的环氧乙烷和未反应的一氧化碳可以经分离并再循环以供用于CSTR中。随后将β-丙内酯产物流从EO/CO分离器供应到图1中描绘为纳米过滤器的羰基化催化剂再循环系统。羰基化催化剂再循环系统被配置成分离存在于β-丙内酯产物流中的残余羰基化催化剂，并且此类经分离的羰基化催化剂可以再循环以供用于CSTR中。图1中所描绘的纳米过滤器可以是任何合适的膜，例如聚合物膜或陶瓷膜，并且产生通常由β-丙内酯、羰基化溶剂、残余羰基化催化剂、少量环氧乙烷、一氧化碳和副产物(例如乙醛和丁二酸酐)组成的保留物流以及通常由β-丙内酯、羰基化溶剂、少量环氧乙烷、一氧化碳、副产物(例如乙醛和丁二酸酐)和痕量的羰基化催化剂组成的渗透物流。在一些实施例中，痕量小于1wt％、小于0.5wt％、小于0.01wt％、小于0.005wt％、小于0.001wt％或小于0.0001wt％。在某些实施例中，痕量低于正使用的测量方法的检测阈值。

[0098] 将渗透物供应到图1中描绘为蒸馏柱的β-丙内酯纯化系统中，其被配置成从溶剂再循环流分离环氧乙烷、一氧化碳和副产物，所述溶剂再循环流描绘为四氢呋喃(THF)再循环流。图1中的系统描绘THF作为羰基化溶剂的用途，但应理解，在其它变化形式中，可使用其它合适的溶剂。将来自β-丙内酯纯化系统的经纯化β-丙内酯流和聚合催化剂供应到图1中描绘为推流式反应器的聚丙内酯生产系统/生产方法中。聚丙内酯生产系统/生产方法被配置成产生聚丙内酯产物流，其可供应到热分解反应器中以产生冰丙烯酸。

[0099] 然而，应理解，虽然图1描绘了一种示范性冰丙烯酸生产系统/生产方法，但是设想了此生产系统的变化形式。举例来说，虽然CSTR描绘为β-丙内酯生产系统/生产方法中的反应器，但是可以采用其它反应器和反应器配置。在另一实例中，虽然在图1中分别描绘了β-丙内酯纯化系统和聚丙内酯生产系统中的蒸馏柱和推流式反应器，但是可以采用其它分离设备以及其它反应器和反应器配置。

[0100] 另外，在本文中所描述的系统的其它示范性实施例中，图1中所描绘的各种单元操作可以组合或省略。在一些变化形式中，β-丙内酯生产系统/生产方法和膜单元操作可以组合(例如膜反应器)，或聚合反应和解聚反应可以组合(例如催化性或反应性蒸馏)，或EO/CO分离器可以省略。

[0101] 另外，应理解，在本文中所描述的系统的其它示范性实施例中，可以采用额外单元操作。举例来说，在一些实施例中，有可能可以将一或多种离子交换树脂并入到系统中以移除可由羰基化催化剂的使用产生的各种阳离子和阴离子催化剂物种。在其它实施例中，一或多个热交换器可并入到系统中以管理和集成在系统中所产生的热。

[0102] 在另外其它实施例中，借以实施所述实施例的方法和/或系统可以采用各种传感器和控制设备来使所述方法和任何相关系统的控制自动化。举例来说，用于所述方法和任何相关系统中的各种反应器，特别是β-丙内酯反应器可以采用传感器来检测在反应器中或进入反应器的水和氧的量。此类传感器可连接到可以调整参数以将水和氧含量维持在预定

量下的控制器。此类传感器可监测羰基化催化剂以检测反应器中水和氧的量，并且可连接到可以控制来自羰基化催化剂源的羰基化催化剂的量的控制器。此外，或替代地，一氧化碳源可包括配置成检测反应器中水和氧的量的传感器，并且此类传感器可以连接到可以控制来自一氧化碳源的一氧化碳的量的控制器。此外，或替代地，环氧乙烷源可包括配置成检测反应器中水和氧的量的传感器，并且此类传感器可连接到可以控制来自环氧乙烷源的环氧乙烷的量的控制器。

[0103] 本文提供配置成用于商业生产聚丙内酯(PPL)和冰丙烯酸(GAA)的各种系统。在一些配置中，PPL和GAA在同一地理位置生产。在其它配置中，PPL在一个位置中生产并运送到生产GAA的第二位置。

[0104] 在此类配置的其它变化形式中，可以在生产系统/生产方法中的各个点处移除残余羰基化催化剂(其可包含阳离子和阴离子物种)。举例来说，在某些配置中，可以在热分解之前从PPL产物流移除残余羰基化催化剂以产生GAA。在其它配置中，如果需要这样做，可以在热分解后通过蒸馏或其它分离装置来移除残余羰基化催化剂。

[0105] 在其它变化形式中，β-丙内酯(bPL)可以借助于bPL的完全转化而聚合以产生PPL。在此类变化形式中，系统中可能不需要额外设备来隔离并再循环bPL到聚合反应器。在其它变化形式中，bPL的转化是不完全的。未反应的bPL可以与PPL产物流分离，并且所回收的bPL可以再循环回到聚合反应器。

[0106] 关于图6到13进一步详细描述系统的配置中的这些变化形式。图6描绘一种示范性系统，其中PPL产物流和GAA产物流在同一位置生产，羰基化催化剂或其组分的至少一部分在进入热分解反应器之前从PPL产物流移除，并且聚丙内酯生产系统/生产方法被配置成实现bPL到PPL的完全转化。

[0107] 羰基化催化剂组分可包含例如由催化剂的降解所产生的化合物、用于产生催化剂的化合物、金属或金属离子(其为催化剂的部分)、任何有机化合物(其为催化剂的部分)、金属羰基或金属络合物(其为催化剂的部分)。举例来说，在一些实施例中，羰基化催化剂组分是羰基钴酸盐、铝沙仑化合物、铝卟啉化合物、铝柳酰醋氨酚化合物、钴或钴离子、或铝或铝离子，或其任何组合。

[0108] BPL生产系统/生产方法(图6中标注为‘羰基化’)通常包含一氧化碳(CO)源、环氧乙烷(EO)源、羰基化催化剂源、溶剂源和羰基化反应器。在某些变化形式中，羰基化反应器被配置成从CO源、EO源和溶剂源(图6中共同标注为‘原料递送’)接收一氧化碳(CO)、环氧乙烷(EO)和溶剂。羰基化反应器进一步被配置成从羰基化催化剂源(图6中标注为‘CO催化剂递送’)接收羰基化催化剂。一氧化碳、环氧乙烷、羰基化溶剂和羰基化催化剂可以通过任何市售源或所属领域中已知的任何市售方法和技术来获得。

[0109] 在一些变化形式中，CO、EO和溶剂基本上不含水和氧。在一种变化形式中，来自溶剂源的溶剂、来自EO源的EO和来自CO源的CO的水和氧浓度小于约500ppm、小于约250ppm、小于约100ppm、小于约50ppm、小于约10ppm、小于约2ppm或小于1ppm。

[0110] 可使用任何合适的羰基化溶剂。在一些实施例中，羰基化溶剂包括四氢呋喃、己烷或其组合。在其它实施例中，羰基化溶剂包括醚、烃或其组合。在另外其它实施例中，羰基化溶剂包括四氢呋喃、四氢吡喃、2,5-二甲基四氢呋喃、环丁砜、N-甲基吡咯烷酮、1,3二甲基-2-咪唑烷酮、二乙二醇二甲醚、三乙二醇二甲醚、四乙二醇二甲醚、二乙二醇二丁醚、异山梨

醇醚、甲基叔丁基醚、二乙醚、二苯醚、1,4-二恶烷、碳酸亚乙酯、碳酸亚丙酯、碳酸亚丁酯、二元酯、二乙醚、乙腈、乙酸乙酯、乙酸丙酯、乙酸丁酯、2-丁酮、环己酮、甲苯、二氟苯、二甲氧基乙烷、丙酮或甲基乙基酮，或其任何组合。在一种变化形式中，羰基化溶剂包括四氢呋喃。

[0111] 本文所用的羰基化催化剂可现场和/或场外制造。在一些实施例中，羰基化催化剂是钴-铝催化剂。在某些实施例中，羰基化催化剂包括与铝卟啉化合物组合的羰基钴酸盐、与铝沙仑化合物组合的羰基钴酸盐或与铝柳酰醋氨酚化合物组合的羰基钴酸盐。在一种变化形式中，羰基化催化剂是(Al(TPP)Co(CO)$_4$)。

[0112] 羰基化反应器可以是连续反应器，例如连续搅拌罐反应器(CSTR)。还可以采用本文中所描述的其它反应器，例如间歇式反应器、推流式反应器(PFR)和半间歇式反应器。

[0113] 再次参考图6中的示范性系统，羰基化反应器可以被配置成以本文中所描述的任何速率、温度或压力从EO源接收EO。举例来说，在一些实施例中，羰基化反应器的入口以约1000kg/hr到25000kg/hr从EO源接收EO。在一些实施例中，羰基化反应器的入口以约30kmol/hr到约500kmol/hr从EO源接收EO。在一些实施例中，羰基化反应器的入口被配置成以介于约10℃与约30℃之间的温度从EO源接收EO。在一些实施例中，羰基化反应器的入口被配置成以介于20巴与约100巴之间和在50巴到70巴的更窄范围内的压力从EO源接收EO。

[0114] 再次参考图6中的示范性系统，羰基化反应器可以被配置成以本文中所描述的任何速率、温度或压力从CO源接收CO。举例来说，在一些实施例中，羰基化反应器的入口被配置成以介于约10℃到约170℃之间和更狭窄地介于10℃到约70℃之间的温度从CO源接收CO。在一些实施例中，羰基化反应器的入口被配置成以介于约20巴与约100巴和更狭窄地50与70巴之间的压力从CO源接收CO。在一些实施例中，将CO供应到羰基化反应器的CO源是新鲜一氧化碳源(即，主要CO进料)或从β-丙内酯生产系统/生产方法再循环的一氧化碳，或其组合。在一些实施例中，新鲜CO源被配置成提供约1000kg/hr CO到约16000kg/hr CO。在一些实施例中，新鲜CO源被配置成提供约30kmol/hr CO到约600kmol/hr CO。在一些实施例中，从β-丙内酯生产系统/生产方法再循环的CO可以提供约100kg/hr CO到约3500kg/hr CO。在一些实施例中，再循环CO源被配置成提供约3kmol/hr CO到约150kmol/hr CO。

[0115] 再次参考图6中的示范性系统，羰基化反应器可以被配置成以本文中所描述的任何速率、温度或压力接收溶剂。举例来说，在一些实施例中，羰基化反应器的入口被配置成以约10000kg/hr到约130000kg/hr的速率从溶剂进料接收溶剂。在一些实施例中，羰基化反应器的入口被配置成以介于约150kmol/hr与约1900kmol/hr之间的速率从溶剂进料接收溶剂。在一些实施例中，羰基化反应器的入口被配置成以介于约10℃与约160℃和更狭窄地10℃与约60℃之间的温度从溶剂进料接收溶剂。在一些实施例中，羰基化反应器的入口被配置成以介于约20巴与约100巴和更狭窄地50与65巴之间的压力从溶剂进料接收溶剂。在一些实施例中，将溶剂供应到羰基化反应器的溶剂进料可包含来自新鲜溶剂源的溶剂、来自BPL纯化系统(例如BPL蒸馏系统)的再循环溶剂和/或来自羰基化催化剂再循环系统的再循环羰基化催化剂流中的溶剂。

[0116] 在一些实施例中，羰基化反应器中的压力为约900psig，并且温度为约70℃。在某些变化形式中，反应器配备有外部冷却器(热交换器)。在一些变化形式中，羰基化反应实现大于99％的bPL选择率。

[0117] 再次参考图6中的示范性系统，β-丙内酯产物流离开羰基化反应器的出口。β-丙内酯产物流包括bPL、溶剂、未反应的EO和CO、羰基化催化剂和副产物，例如乙醛副产物(ACH)和丁二酸酐(SAH)。β-丙内酯产物流可具有本文中所描述的bPL、溶剂、EO、CO、羰基化催化剂、ACH和SAH的任何浓度。举例来说，在一些实施例中，β-丙内酯产物流包含约2000kg/hr bPL到约40000kg/hr bPL。在一些实施例中，β-丙内酯产物流包含约30kmol/hr bPL到约550kmol/hr bPL。在一些实施例中，β-丙内酯产物流中的bPL的质量分数可为约0.1到约0.4。在一些实施例中，β-丙内酯产物流中的bPL的摩尔分数可为约0.1到约0.6，和更狭窄地0.1到0.4。β-丙内酯产物流还可包含其它组分，包含未反应的环氧乙烷(呈约0.005到0.15，或至多约0.1的质量分数)、未反应的一氧化碳(呈约0.0005到0.04，或至多约0.02的质量分数)、乙醛(呈约0.0005到0.01，或至多约0.02的质量分数)、丁二酸酐(呈约0.0005到0.005，或至多约0.01的质量分数)、羰基化催化剂(呈约40到640kg/hr，或至多约600kg/hr；或呈约0.001到0.005，或至多约0.004的质量分数)和剩余物溶剂。在一些实施例中，β-丙内酯产物流包括羰基化催化剂组分(呈约40到640kg/hr，或至多约600kg/hr；或呈约0.001到0.005，或至多约0.004的质量分数)。在一些实施例中，来自β-丙内酯生产系统/生产方法的β-丙内酯产物流可具有约40℃或50℃到约100℃的温度和约1巴到约15巴或更狭窄地到5巴的压力。

[0118] 再次参考图6中的示范性系统，β-丙内酯产物流从羰基化反应器的出口输出并且进入环氧乙烷和一氧化碳分离器(图6中的标注为‘EO/CO’)的入口。在一个实施例中，环氧乙烷和一氧化碳分离器是闪蒸罐。大部分环氧乙烷和一氧化碳从羰基化反应流再循环，并且可再循环回到羰基化反应器作为再循环乙烯氧化物流和再循环一氧化碳流(图6中标注为‘再循环’)，或将其送出以供处理(图6中标注为‘燃烧’)。在一些实施例中，将羰基化反应流中至少10％的环氧乙烷和80％的一氧化碳回收。再循环一氧化碳流还可包含未反应的环氧乙烷(呈至多约250kg/hr或呈介于约0.05与约0.075之间的质量分数)、次级反应产物乙醛(呈至多约13kg/hr或呈约0.001到约0.009的质量分数)、bPL(呈至多约0.19kg/hr)和剩余物溶剂(例如THF)。

[0119] 再次参考图6中的示范性系统，β-丙内酯产物流泵送到羰基化催化剂再循环系统中。在一些变化形式中，环氧乙烷和一氧化碳使用除燃烧以外的方法来处理。举例来说，在一个实施例中，从β-丙内酯产物流回收的环氧乙烷和一氧化碳使用焚烧来处理。

[0120] 再次参考图6中的示范性系统，β-丙内酯产物流进入羰基化催化剂再循环系统的入口。羰基化催化剂再循环系统可以被配置成使用本文中所描述的方法中的任一个来使羰基化催化剂的至少一部分与β-丙内酯产物流隔离，所述方法包含例如蒸馏、液-液萃取、离子液体、纳米过滤、离子交换或吸附，或其任何组合。在一些变化形式中，羰基化催化剂再循环系统包含膜分离器。在某些变化形式中，膜分离器包括聚合物膜，而在其它变化形式中，膜分离器包括陶瓷膜。在一些变化形式中催化剂再循环系统的膜被配置成实现90％到100％的催化剂排出，并且渗透率大于1。在一些实施例中，膜实现大于90％、92％、95％、98％或99％的催化剂排出。

[0121] 羰基化催化剂再循环系统被配置成产生再循环羰基化催化剂流(图6中标注为‘保留物’)，其包括bPL、溶剂、环氧乙烷、一氧化碳、副产物(例如乙醛和羰基化催化剂)和羰基化催化剂；以及后隔离β-丙内酯产物流(图6中标注为‘渗透物’)，其包括bPL、溶剂、环氧乙

烷、一氧化碳、副产物(例如乙醛和丁二酸酐)和痕量的羰基化催化剂。在一些实施例中,后隔离β丙内酯产物流包括痕量的羰基化催化剂组分。在一些实施例中,痕量小于1wt%、小于0.5wt%、小于0.01wt%、小于0.005wt%、小于0.001wt%或小于0.0001wt%。在某些实施例中,痕量低于正使用的测量方法的检测阈值。

[0122] 再循环羰基化催化剂流可包括本文中所揭示的任何浓度的羰基化催化剂、羰基化催化剂组分和溶剂。举例来说,在一些实施例中,再循环羰基化催化剂流中的羰基化催化剂的质量分数为约0.005到约0.05。在一些实施例中,再循环羰基化催化剂流中的羰基化催化剂组分的质量分数为约0.0051到约0.05。在一些实施例中,再循环羰基化催化剂流中的羰基化催化剂的摩尔分数为约0.0005到约0.05。在一些实施例中,再循环羰基化催化剂流中的羰基化催化剂组分的摩尔分数为约0.0005到约0.05。在一些实施例中,再循环羰基化催化剂流中的溶剂的质量分数介于0.60与约0.99之间。在一些实施例中,再循环羰基化催化剂流中的溶剂的摩尔分数介于约0.60与约0.99之间。在一些实施例中,再循环羰基化催化剂流还可包含未反应的一氧化碳(呈至多约15kg/hr或呈至多约0.001的质量分数)、未反应的环氧乙烷(呈至多约330kg/hr或呈介于0.005与0.01之间的质量分数)、次级反应产物乙醛(呈至多约33kg/hr或呈至多约0.001的质量分数)、次级反应产物丁二酸酐(呈至多约30kg/hr或呈至多约0.001的质量分数)、bPL(呈至多约5450kg/hr或呈至多约0.25的质量分数)。再循环羰基化催化剂流再循环回到羰基化反应器。

[0123] 后隔离β-丙内酯产物流可具有本文中所描述的任何浓度的bPL、溶剂、环氧乙烷、一氧化碳、副产物(例如乙醛和丁二酸酐)、羰基化催化剂或羰基化催化剂组分。举例来说,在一些实施例中,后隔离β-丙内酯产物流包含约2000kg/hr bPL到约35000kg/hr bPL。在一些实施例中,后隔离β-丙内酯产物流包含约30kmol/hr bPL到约450kmol/hr bPL。在一些实施例中,后隔离β-丙内酯产物流中的bPL的质量分数可为约0.1到0.4,或后隔离β-丙内酯产物流中的bPL的摩尔分数可为约0.1到约0.4。后隔离β-丙内酯产物流还可包含其它组分,包含未反应的环氧乙烷(呈约0.005到0.1的质量分数)、未反应的一氧化碳(呈约0.0005到0.001,或至多约0.002的质量分数)、乙醛(呈约0.0005到0.001,或至多约0.002的质量分数)、丁二酸酐(呈约0.0005到0.01,或至多约0.02的分数)、羰基化催化剂(呈约0到50kg/hr,或至多约20kg/hr)、羰基化催化剂组分(呈约0到50kg/hr,或至多约20kg/hr)和剩余物溶剂。在一些实施例中,来自羰基化催化剂再循环系统的后隔离β-丙内酯产物流的温度为约20℃到约60℃。在一些实施例中,后隔离β-丙内酯产物流的压力可为约1到约5巴。

[0124] 再次参考图6中的示范性系统,后隔离β-丙内酯产物流可以进入BPL纯化系统(图6中标注为'BPL蒸馏')的入口。在一种变化形式中,BPL纯化系统包括以或以低于大气压操作的被配置成产生回收溶剂流的一或多个蒸馏柱,以及包括纯化bPL和痕量的羰基化催化剂(图6中标注为'BPL/残余催化剂')的生产流。以此方式选择压力来达到降低bPL分解的温度。在一些实施例中,一或多个蒸馏柱在约0.15绝对巴的压力和介于约80℃与约120℃之间的温度下操作。在一些实施例中,蒸馏系统被配置成产生基本上不含环氧乙烷、一氧化碳、乙醛和丁二酸酐的再循环溶剂流。

[0125] 再次参考图6中的示范性系统,回收溶剂流离开BPL纯化系统的出口且可供应回到羰基化反应器。在一些变化形式中,在供应到羰基化反应器之前减低再循环溶剂流中H_2O和O_2的浓度。回收溶剂流在供应回到羰基化反应器时可具有本文中所描述的任何浓度的H_2O和

O_2。举例来说，在一些实施例中，在供应回到羰基化反应器中时H_2O和O_2的浓度小于约500ppm、小于约250ppm、小于约100ppm、小于约50ppm、小于约20ppm、小于约10ppm、小于约2ppm或小于约1ppm。

[0126] 再次参考图6中的示范性系统，包括纯化bPL的生产流离开BPL纯化系统的出口。生产流可含有痕量的羰基化催化剂，但基本上不含溶剂、环氧乙烷、一氧化碳、乙醛和丁二酸酐。在一些实施例中，生产流含有质量分数为约0.90到1.0的bPL。在一些实施例中，生产流中bPL的摩尔分数为约0.90到1.0。在一些实施例中，生产流的剩余物包含例如丁二酸酐等次级反应产物(呈至多约0.015或0到0.0015的摩尔分数)、剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，生产流的剩余物包含羰基化催化剂组分(呈至多约1000ppm)。

[0127] 生产流进入聚丙内酯生产系统/生产方法的入口。在图6中所描绘的示范性系统中，聚丙内酯生产系统/生产方法包括聚合反应器(图6中标注为‘聚合’)。聚丙内酯生产系统/生产方法被配置成以本文中所描述的任何速率、浓度、温度或压力接收和输出流。举例来说，在一个实施例中，聚合方法的入口可包含约2000kg/hr bPL到约35000kg/hr bPL。在一些实施例中，聚合方法的入口可包含约25kmol/hr bPL到约500kmol/hr bPL。在一些实施例中，聚合方法的入口中bPL的质量分数可为约0.90到1.0。在一些实施例中，聚合方法的入口中bPL的摩尔分数可为约0.90到1.0。进入聚合方法的生产流的剩余物可包含例如丁二酸酐等次级反应产物(呈至多约0.015或0到约0.015的摩尔分数)、剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。进入聚合方法的生产流的剩余物可包含羰基化催化剂组分(呈至多约1000ppm)。在一些实施例中，聚合方法的入口还可包含聚合催化剂，例如在聚合反应是均相聚合反应的情况下。在一些实施例中，进入聚合方法的生产流的温度可介于约80℃与120℃之间。在一些实施例中，离开蒸馏方法的生产流可处于约0.05巴到约0.15巴的压力下。在一些实施例中，进入聚合方法的生产流可处于至少约0.05巴、至少约1巴或至少约5巴或介于约0.05巴与约20巴之间的压力下。

[0128] 再次参考图6中的示范性系统，聚丙内酯生产系统/生产方法被配置成以连续模式操作，并且实现生产流中的bPL到PPL的完全转化。PPL产物流(图6中标注为‘PPL/残余催化剂’)离开聚丙内酯生产系统/生产方法的出口，并且包括具有痕量羰基化催化剂的PPL。在一些实施例中，PPL产物流包括痕量的羰基化催化剂组分。

[0129] 在一些实施例中，聚合方法被配置成产生约2000kg/hr PPL到约35000kg/hr PPL。在一些实施例中，聚合方法被配置成产生约25kmol/hr PPL到约500kmol/hr PPL。

[0130] 在一些实施例中，PPL产物流中PPL的质量分数可为约0.90到1.0。在一些实施例中，PPL产物流中PPL的摩尔分数可为约0.90到1.0。PPL产物流的剩余物可包含未反应的bPL(呈至多约0.02或介于0与0.02之间的摩尔分数)、例如丁二酸酐等次级反应产物(呈至多约0.01或介于0与0.01之间的摩尔分数)、和剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，PPL产物流的剩余物可包含羰基化催化剂组分(呈至多约1000ppm)。在一些实施例中，PPL产物流的温度可介于约100℃与140℃之间。在一些实施例中，PPL产物流可处于至少约0.001巴的压力下。

[0131] 再次参考图6中的示范性系统，PPL产物流进入PPL纯化系统的入口(图6中标注为‘IER’)。PPL纯化系统可包括被配置成减小PPL产物流中羰基化催化剂的浓度的离子交换树

脂(IER)。阳离子和阴离子羰基化催化剂物种从PPL纯化系统中的IER回收,并且可再生以获得可用于再循环到羰基化反应器的催化剂或被处理(图6中标注为‘再生/处理’)。后纯化PPL产物流离开PPL纯化系统的出口并进入热分解反应器的入口。后纯化PPL产物流可具有本文中所描述的任何化合物浓度、温度或压力。举例来说,在一些实施例中,后纯化PPL产物流中PPL的质量分数可为约0.90到1.0。在一些实施例中,后纯化PPL产物流中PPL的摩尔分数可为约0.90到1.0。在一些实施例中,后纯化PPL产物流的温度可介于约100℃与140℃之间。在一些实施例中,后纯化PPL产物流可处于至少约0.001巴的压力下。

[0132] 再次参考图6中的示范性系统,热分解反应器被配置成将后纯化PPL流转化成GAA产物流。在一些实施例中,热分解反应器的温度介于140℃或160℃与300℃之间并且压力介于0.1绝对巴与5绝对巴之间。

[0133] 痕量的高沸点有机杂质(图6中标注为‘有机重组分’)与GAA流分离,离开热分解反应器的出口,并且传送到焚化炉以供处理(图6中标注为‘焚烧炉’)。

[0134] GAA产物流离开热分解反应器的出口以供用于存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中,GAA产物流的温度可介于约15℃与约50℃之间。在一些实施例中,GAA产物流可处于约0.5巴到约1.5巴的压力下。

[0135] 图6中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说,在一些实施例中,所述系统生产至少约25千吨每年(“KTA”)到约250KTA,以供进行约8000小时的年生产操作。在一些实施例中,生产系统/生产方法可产生至少约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中,生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0136] 图7提供一种示范性生产系统/生产方法,其中PPL产物流和GAA产物流在同一位置生产,羰基化催化剂或其组分的至少一部分在进入热分解反应器之前从PPL产物流移除,并且在聚合反应器中生产流中的bPL到PPL的转化是不完全的,其中将bPL再循环回到聚合反应器。图7中所示的生产系统/生产方法具有与图6中所示的羰基化反应器、CO催化剂再循环系统、EO/CO再循环系统和BPL纯化系统的配置相同的配置。

[0137] 再次参考图7中的示范性系统,包括纯化bPL的生产流离开BPL纯化系统的出口。生产流可含有痕量的羰基化催化剂,但基本上不含溶剂、环氧乙烷、一氧化碳、乙醛和丁二酸酐。在一些实施例中,生产流含有质量分数为约0.90到1.0的bPL。在一些实施例中,生产流中bPL的摩尔分数为约0.90到1.0。在一些实施例中,生产流的剩余物包含例如丁二酸酐的次级反应产物(呈至多约0.015的摩尔分数)、剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中,生产流的剩余物包含羰基化催化剂组分(呈至多约1000ppm)。

[0138] 再次参考图7中的示范性系统,聚丙内酯生产系统/生产方法包括聚合反应器(图7中标注为‘聚合’)和BPL再循环系统(图7中标注为‘蒸馏/WFE’)。聚丙内酯生产系统/生产方法可以被配置成以本文中所描述的生产流的任何速率、浓度、温度或压力接收和输出流。举例来说,在一个实施例中,聚合方法的入口可包含约2000kg/hr bPL到约35000kg/hr bPL。在一些实施例中,聚合方法的入口可包含约25kmol/hr bPL到约500kmol/hr bPL。在一些实

施例中，聚合方法的入口中bPL的质量分数可为约0.90到1.0。在一些实施例中，聚合方法的入口中bPL的摩尔分数可为约0.90到1.0。进入聚合方法的生产流的剩余物可包含例如丁二酸酐等次级反应产物(呈至多约0.015或0到0.015的摩尔分数)、和剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，进入聚合方法的生产流的剩余物可包含羰基化催化剂组分(呈至多约1000ppm)。在一些实施例中，聚合方法的入口还可包含聚合催化剂，例如在聚合反应是均相聚合反应的情况下。在一些实施例中，进入聚合方法的生产流的温度可介于约80与120℃之间。在一些实施例中，进入聚合方法的生产流可处于约0.05巴到约20巴的压力下。

[0139] 再次参考图7中的示范性系统，PPL生产系统/生产方法被配置成以连续模式操作，从而实现bPL到PPL的部分转化。PPL生产系统/生产方法可以被配置成实现各种程度的bPL转化。举例来说，在一些实施例中，生产流中至少40％、至少50％、至少60％、至少70％、至少80％或至少90％的bPL转化成PPL。在一些实施例中，生产流中约50％到约99％的bPL转化成PPL。部分聚合流离开聚合反应器的出口并进入BPL再循环系统的入口。BPL再循环系统被配置成将未反应的bPL与部分聚合流分离并且将bPL再循环回到聚合反应器中(图7中标注为‘bPL’)。在一些实施例中，BPL再循环系统包括一或多个蒸馏柱，而在其它实施例中，BPL再循环系统包括一或多个刮膜式蒸发器(WFE)。PPL产物流(图7中标注为‘PPL/残余催化剂’)离开BPL再循环系统的出口，且包括具有痕量的羰基化催化剂的PPL。在一些实施例中，PPL产物流包括具有痕量的羰基化催化剂组分的PPL。在一些实施例中，聚合方法可产生约2000kg/hr PPL到约35000kg/hr PPL。在一些实施例中，聚合方法可产生约25kmol/hr PPL到约500kmol/hr PPL。

[0140] 在一些实施例中，PPL产物流中PPL的质量分数可为约0.90到1.0。在一些实施例中，PPL产物流中PPL的摩尔分数可为约0.90到1.0。PPL产物流的剩余物可包含未反应的bPL(呈至多约0.02或0到0.02的摩尔分数)、例如丁二酸酐等次级反应产物(呈至多约0.01或0到0.01的摩尔分数)、和剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，PPL产物流的剩余物可包含羰基化催化剂组分(呈至多约1000ppm)。在一些实施例中，PPL产物流的温度可介于约100℃与140℃之间。在一些实施例中，PPL产物流可处于至少约0.001巴的压力下。

[0141] PPL产物流进入PPL纯化系统的入口(图7中标注为‘IER’)。在一些变化形式中，PPL纯化系统可使用离子交换树脂(IER)来减小PPL产物流中羰基化催化剂的浓度。阳离子和阴离子羰基化催化剂物种从PPL纯化系统中的IER回收，并且可再生以获得可用于再循环到羰基化反应器的催化剂或被处理(图7中标注为‘再生/处理’)。后纯化PPL产物流离开PPL纯化系统的出口并进入热分解反应器的入口。后纯化PPL产物流可具有本文中所描述的任何化合物浓度、温度或压力。举例来说，在一些实施例中，后纯化PPL产物流中PPL的质量分数可为约0.90到1.0。在一些实施例中，后纯化PPL产物流中PPL的摩尔分数可为约0.90到1.0。在一些实施例中，后纯化PPL产物流的温度可介于约100℃与约140℃之间。在一些实施例中，后纯化PPL产物流可处于至少约0.001巴的压力下。

[0142] 再次参考图7中的示范性系统，冰丙烯酸生产系统/生产方法被配置成将后纯化PPL流转化成GAA流。痕量的高沸点有机杂质(图7中标注为‘有机重组分’)经由热分解反应器的出口输出，并传送到焚烧炉以供处理(图7中标注为‘焚烧炉’)。GAA产物流离开热分解

反应器的出口，且可经冷凝、进一步加工或存储。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA产物流可处于约0.5巴到约1.5巴的压力下。

[0143] 图7中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，所述系统生产至少约25千吨每年(“KTA”)到约400KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0144] 图8描绘一种示范性生产系统/生产方法，其中PPL产物流和GAA产物流在同一位置生产，羰基化催化剂或其组分在进入热分解反应器之前不从PPL产物流移除，聚合方法中bPL到PPL的转化是完全的，其中不将bPL再循环到聚合方法，并且羰基化催化剂或其组分从由热分解反应器产生的有机重组分移除。图8中所示的生产系统/生产方法具有与图6中所示的羰基化反应器、CO催化剂再循环系统、EO/CO再循环系统和BPL纯化系统的配置相同的配置。

[0145] 再次参考图8中的示范性系统，生产流离开BPL纯化系统的出口并进入聚合方法的入口。在图8中所描绘的生产系统/生产方法中，聚合方法包括聚合反应器(图8中标注为‘聚合’)。聚合方法的入口可包含本文中所描述的生产流的任何速率、浓度、温度或压力。举例来说，在一个实施例中，聚合方法的入口可包含约2000kg/hr bPL到约35000kg/hr bPL。在一些实施例中，聚合方法的入口可包含约25kmol/hr bPL到约500kmol/hr bPL。在一些实施例中，聚合方法的入口中bPL的质量分数可为约0.90到1.0。在一些实施例中，聚合方法的入口中bPL的摩尔分数可为约0.90到1.0。进入聚合方法的生产流的剩余物可包含例如丁二酸酐等次级反应产物(呈至多约0.015或0到0.015的摩尔分数)、剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，进入聚合方法的生产流的剩余物可包含羰基化催化剂组分(呈至多约1000ppm)。在一些实施例中，聚合方法的入口还可包含聚合催化剂，例如在聚合反应是均相聚合反应的情况下。在一些实施例中，进入聚合方法的生产流的温度可介于约80℃与约120℃之间。在一些实施例中，进入聚合方法的生产流可处于约0.05巴到约0.15巴的压力下。

[0146] 再次参考图8中的示范性系统，聚丙内酯生产系统/生产方法被配置成以连续模式操作，从而实现生产流中的bPL到PPL的完全转化。PPL产物流(图8中标注为‘PPL/残余催化剂’)离开聚合方法出口，且包括具有痕量的羰基化催化剂的PPL。在一些实施例中，PPL产物流包括具有痕量的羰基化催化剂组分的PPL。

[0147] 在一些实施例中，聚合方法可产生约2000kg/hr PPL到约35000kg/hr PPL。在一些实施例中，聚合方法可产生约25kmol/hr PPL到约500kmol/hr PPL。

[0148] 在一些实施例中，PPL产物流中PPL的质量分数可为约0.90到1.0。在一些实施例中，PPL产物流中PPL的摩尔分数可为约0.90到1.0。PPL产物流的剩余物可包含未反应的bPL(呈至多约0.02或0到0.02的摩尔分数)、例如丁二酸酐的次级反应产物(呈至多约0.01或0到0.01的摩尔分数)、剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，PPL产物流的温度可介于约100℃与约140℃之间。在一些实施例中，PPL产物流可

处于至少约0.001巴的压力下。

[0149] 再次参考图8中的示范性系统，PPL产物流进入热分解反应器的入口。热分解反应器被配置成将PPL产物流转化成GAA流。痕量的高沸点有机杂质(图8中标注为‘有机重组分’)经由热分解反应器的出口输出。高沸点有机杂质流进入包括离子交换树脂(IER)的纯化系统(图8中标注为‘IER’)，所述离子交换树脂可用于一些实施例中。IER被配置成减小高沸点有机杂质流中的羰基化催化剂的浓度。在一些实施例中，高沸点有机杂质流中的羰基化催化剂的浓度在进入纯化系统之前介于100ppm与1000ppm之间，并且在离开纯化系统后小于50ppm、小于20ppm或小于5ppm。

[0150] 阳离子和阴离子羰基化催化剂物种从IER回收，且可再生以获得可用于再循环到羰基化反应器的催化剂或被处理(图8中标注为‘再生/处理’)。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA产物流可处于约0.5到约1.5巴的压力下。

[0151] 图8中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，系统生产至少约25千吨每年(“KTA”)或约25KTA到约400KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0152] 图9描绘一种示范性生产系统/生产方法，其中PPL产物流和GAA产物流在同一位置生产，羰基化催化剂或其组分在进入热分解反应器之前不从PPL产物流移除，聚合方法中bPL到PPL的转化是不完全的并将bPL再循环到聚合方法，并且羰基化催化剂或其组分从由热分解反应器产生的有机重组分移除。图9中所示的生产系统/生产方法具有与图6中所示的羰基化反应器、CO催化剂再循环系统、EO/CO再循环系统和BPL纯化系统的配置相同的配置。

[0153] 再次参考图9中的示范性系统，包括纯化bPL的生产流离开BPL纯化系统的出口。生产流含有痕量的羰基化催化剂，但基本上不含THF、EO、CO、ACH和SAH。将生产流前向供应并进入聚合方法的入口。聚合方法包括聚合反应器(图9中标注为‘聚合’)和BPL再循环系统(图9中标注为‘蒸馏/WFE’)。聚合方法的入口可包含本文中所描述的生产流的任何速率、浓度、温度或压力。举例来说，在一个实施例中，聚合方法的入口可包含约2000kg/hr bPL到约35000kg/hr bPL。在一些实施例中，聚合方法的入口可包含约25kmol/hr bPL到约500kmol/hr bPL。在一些实施例中，聚合方法的入口中bPL的质量分数可为约0.90到1.0。在一些实施例中，聚合方法的入口中bPL的摩尔分数可为约0.90到1.0。进入聚合方法的生产流的剩余物可包含例如丁二酸酐等次级反应产物(呈至多约0.015或0到0.015的摩尔分数)、和剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，聚合方法的入口还可包含聚合催化剂，例如在聚合反应是均相聚合反应的情况下。在一些实施例中，进入聚合方法的生产流的温度可介于约80℃与120℃之间。在一些实施例中，进入聚合方法的生

产流可处于约0.05巴到约20巴的压力下。

[0154] 再次参考图9中的示范性系统，聚丙内酯生产系统/生产方法被配置成以连续模式操作，从而实现生产流中的bPL到PPL的部分转化。聚丙内酯生产系统/生产方法可以被配置成实现各种程度的bPL转化。举例来说，在一些实施例中，生产流中至少40％、至少50％、至少60％、至少70％、至少80％或至少90％的bPL转化成PPL。在一些实施例中，生产流中约50％到约95％的bPL转化成PPL。在一些实施例中，生产流中约50％到约99％的bPL转化成PPL。部分聚合流离开聚合反应器的出口并进入BPL再循环系统的入口。BPL再循环系统被配置成将未反应的bPL与部分聚合流分离并且将bPL再循环回到聚合反应器中(图9中标注为‘bPL’)。在一些实施例中，BPL再循环系统包括一或多个蒸馏柱，而在其它实施例中，BPL再循环系统包括一或多个刮膜式蒸发器(WFE)。PPL产物流(图9中标注为‘PPL/残余催化剂’)离开BPL再循环系统的出口，且包括具有痕量的羰基化催化剂的PPL。在一些实施例中，PPL产物流包括具有痕量的羰基化催化剂组分的PPL。在一些实施例中，聚合方法被配置成产生约2000kg/hr PPL到约35000kg/hr PPL。在一些实施例中，聚合方法被配置成产生约25kmol/hr PPL到约500kmol/hr PPL。

[0155] 在一些实施例中，PPL产物流中PPL的质量分数可为约0.90到1.0。在一些实施例中，PPL产物流中PPL的摩尔分数可为约0.90到1.0。PPL产物流的剩余物可包含未反应的bPL(呈至多约0.02或0到0.02的摩尔分数)、例如丁二酸酐等次级反应产物(呈至多约0.01或0到0.01的摩尔分数)、剩余溶剂(例如THF)和剩余羰基化催化剂(呈至多约1000ppm)。在一些实施例中，PPL产物流的温度可介于约100℃与140℃之间。在一些实施例中，PPL产物流可处于至少约0.001巴的压力下。

[0156] 再次参考图9中的示范性系统，PPL产物流进入热分解反应器的入口。热分解反应器被配置成将PPL产物流转化成GAA流。痕量的高沸点有机杂质(图9中标注为‘有机重组分’)经由热分解反应器的出口输出。高沸点有机杂质流进入包括离子交换树脂(IER)的纯化系统(图9中标注为‘IER’)。IER被配置成减小高沸点有机杂质流中的羰基化催化剂(或其组分)的浓度。阳离子和阴离子羰基化催化剂物种从IER回收，且可再生以获得可用于再循环到羰基化反应器的催化剂或被处理(图9中标注为‘再生/处理’)。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA产物流可处于约0.5到约1.5巴的压力下。

[0157] 图9中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，系统生产至少约25千吨每年(“KTA”)，或约25KTA到约400KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0158] 图10描绘另一示范性生产系统/生产方法，其中PPL产物流在第一位置生产，随后经隔离、包装并运送到生产GAA产物流的第二位置；羰基化催化剂或其组分在进入热分解反应器之前从PPL产物流移除，聚合反应器实现生产流中的bPL到PPL的完全转化，并且bPL不

再循环回到聚合反应器。图10中的生产系统/生产方法具有与图6所示的羰基化反应器、CO催化剂再循环系统、EO/CO再循环系统和BPL纯化系统、聚合方法、PPL纯化系统以及再生或处理羰基化催化剂组分的配置相同的配置。

[0159] 再次参考图10中的示范性系统，后纯化PPL产物流离开PPL纯化系统的出口，且以所属领域中已知的任何方法在基本上干燥的氛围中粒化、挤压、成片、成粉末或形成颗粒。固体后纯化PPL产物流随后前向供应到包装，且准备好运送到GAA生产系统/生产方法的位置。选择用于运送固体后纯化PPL产物流的包装来利用固体PPL使水分吸收降到最低。在GAA生产系统/生产方法的位置处，基本上纯的、基本上干燥的固体后纯化PPL产物流以使水分引入降到最低的方式打开包装，且随后以固体或熔融形式供应到热分解反应器的入口。热分解反应器被配置成将后隔离PPL产物流转化成GAA流。痕量的高沸点有机杂质(图10中标注为‘有机重组分’)经由热分解反应器的出口输出并传送到焚烧炉以供处理(图10中标注为‘焚烧炉’)。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA产物流可处于约0.5到约1.5巴的压力下。

[0160] 图10中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，系统生产至少约25千吨每年(“KTA”)，或约25KTA到约400KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0161] 图11描绘一种示范性生产系统/生产方法，其中PPL产物流在第一位置生产，随后经隔离、包装并运送到生产GAA产物流的第二位置；羰基化催化剂或其组分在进入热分解反应器之前从PPL产物流移除，聚合反应器实现生产流中的bPL到PPL的不完全转化，并且bPL再循环回到聚合反应器。图11中的生产系统/生产方法具有与图7所示的羰基化反应器、CO催化剂再循环系统、EO/CO再循环系统和BPL纯化系统、聚合方法、PPL纯化系统以及再生或处理羰基化催化剂组分的配置相同的配置。

[0162] 再次参考图11中的示范性系统，后纯化PPL产物流离开PPL纯化系统的出口，且以所属领域中已知的任何方法在基本上干燥的氛围中粒化、挤压、成片、成粉末或形成颗粒。固体后纯化PPL产物流随后前向供应到包装，且准备好运送到GAA生产系统/生产方法的位置。选择用于运送固体后纯化PPL产物流的包装来利用固体PPL使水分吸收降到最低。在GAA生产系统/生产方法的位置处，基本上纯的、基本上干燥的固体后纯化PPL产物流以使水分引入降到最低的方式打开包装，且随后以固体或熔融形式供应到热分解反应器的入口。热分解反应器被配置成将后隔离PPL产物流转化成GAA流。痕量的高沸点有机杂质(图11中标注为‘有机重组分’)经由热分解反应器的出口输出并传送到焚烧炉以供处理(图11中标注为‘焚烧炉’)。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA

产物流可处于约0.5到约1.5巴的压力下。

[0163] 图11中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，系统生产至少约25千吨每年(“KTA”)，或约25KTA到约250KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0164] 图12描绘另一示范性生产系统/生产方法，其中PPL产物流在第一位置处生产，随后经隔离、包装并运送到生产GAA产物流的第二位置；羰基化催化剂或其组分在进入热分解反应器之前不从PPL产物流移除；聚合反应器实现生产流中的bPL到PPL的完全转化且bPL不再循环回到聚合反应器；并且羰基化催化剂或其组分从由热分解反应器生产的有机重组分移除。图12中的生产系统/生产方法具有与图8中所示的羰基化反应器、CO催化剂再循环系统、EO/CO再循环系统和BPL纯化系统以及聚合方法的配置相同的配置。

[0165] 再次参考图12中的示范性系统，PPL产物流离开聚合方法的出口，且以所属领域中已知的任何方法在基本上干燥的氛围中粒化、挤压、成片、成粉末或形成颗粒。固体PPL产物流随后前向供应到包装，且准备好运送到GAA生产系统/生产方法的位置。选择用于运送固体PPL产物流的包装来利用固体PPL使水分吸收降到最低。在GAA生产系统/生产方法的位置处，基本上纯的、基本上干燥的固体PPL产物流以使水分引入降到最低的方式打开包装，且随后以固体或熔融形式供应到热分解反应器的入口。热分解反应器被配置成将PPL产物流转化成GAA流。痕量的高沸点有机杂质(图12中标注为‘有机重组分’)经由热分解反应器的出口输出。高沸点有机杂质流进入包括离子交换树脂(IER)的纯化系统(图12中标注为‘IER’)，所述离子交换树脂是可采用的一个分离的实例。IER被配置成减小高沸点有机杂质流中的羰基化催化剂(或其组分)的浓度。阳离子和阴离子羰基化催化剂物种从IER回收，且可再生以获得可用于再循环到羰基化反应器的催化剂或被处理(图12中标注为‘再生/处理’)。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。在优选实施例中，控制温度以限制丙烯酸自动聚合的风险。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA产物流可处于约0.5到约1.5巴的压力下。

[0166] 图12中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，系统生产至少约25千吨每年(“KTA”)，或约25KTA到约400KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0167] 图13描绘一种示范性生产系统/生产方法，其中PPL产物流在第一位置处生产，随后经隔离、包装并运送到生产GAA产物流的第二位置；羰基化催化剂或其组分在进入热分解反应器之前不从PPL产物流移除；聚合反应器实现生产流中的bPL到PPL的不完全转化且bPL再循环回到聚合反应器；并且羰基化催化剂或其组分从由热分解反应器生产的有机重组分移除。图13中的生产系统/生产方法具有与图9中所示的羰基化反应器、CO催化剂再循环系

统、EO/CO再循环系统和BPL纯化系统以及聚合方法的配置相同的配置。

[0168] 再次参考图13中的示范性系统，PPL产物流离开聚合方法的出口，且以所属领域中已知的任何方法在基本上干燥的氛围中粒化、挤压、成片、成粉末或形成颗粒。固体PPL产物流随后前向供应到包装，且准备好运送到GAA生产系统/生产方法的位置。选择用于运送固体PPL产物流的包装来利用固体PPL使水分吸收降到最低。在GAA生产系统/生产方法的位置处，基本上纯的、基本上干燥的固体PPL产物流以使水分引入降到最低的方式打开包装，且随后以固体或熔融形式供应到热分解反应器的入口。热分解反应器被配置成将PPL产物流转化成GAA流。痕量的高沸点有机杂质(图13中标注为‘有机重组分’)经由热分解反应器的出口输出。高沸点有机杂质流进入包括离子交换树脂(IER)的纯化系统(图13中标注为‘IER’)。IER被配置成减小高沸点有机杂质流中的羰基化催化剂(或其组分)的浓度。阳离子和阴离子羰基化催化剂物种从IER回收，且可再生以获得可用于再循环到羰基化反应器的催化剂或被处理(图13中标注为‘再生/处理’)。GAA产物流离开热分解反应器的出口以供存储或进一步加工。GAA产物流包括基本上纯的GAA。GAA产物流可以本文中所描述的任何速率、浓度、温度或压力离开热分解反应器的出口。GAA产物流的剩余物可包含例如丁二酸酐等次级反应产物和例如THF等剩余溶剂。在一些实施例中，GAA产物流的温度可介于约15℃与约60℃之间。在一些实施例中，GAA产物流可处于约0.5到约1.5巴的压力下。

[0169] 图13中所描绘的示范性生产系统/生产方法可以本文中所描述的任何速率产生GAA。举例来说，在一些实施例中，系统生产至少约25千吨每年(“KTA”)、至少约100KTA、至少约110KTA、至少约120KTA、至少约130KTA、至少约140KTA、至少约150KTA、至少约160KTA、至少约170KTA、至少约180KTA、至少约190KTA、至少约200KTA、至少约250KTA、至少约300KTA、至少约350KTA、至少约400KTA，和在可与前述变化形式中的任一个组合的一些变化形式中，高达约400KTA，以供进行约8000小时的年生产操作。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA，或约2000kg/hr GAA到约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约25kmol/hr GAA到约500kmol/hr GAA。

[0170] 应理解，虽然图6到13描绘包括一定步骤和单元操作的方法配置，但是在本文中所描述的方法的其它实施例中，方法配置含有更少步骤、更多步骤、更少单元操作或更多单元操作。举例来说，在一些变化形式中，渗透物流经处理以在BPL纯化组列之前移除痕量羰基化催化剂的至少一部分。在某些变化形式中，有可能可以利用离子交换树脂从渗透物移除痕量羰基化催化剂的至少一部分。因此，在某些实施例中，图6到13中的方法配置包含在渗透物进入BPL纯化组列之前使用IER从渗透物移除痕量羰基化催化剂的至少一部分的额外步骤。在一些实施例中，图6到13中所描绘的和本文中所描述的系统包含BPL纯化组列之前的具有IER的纯化系统。在其它实施例中，系统包含BPL纯化组列之前的具有IER的纯化系统且在聚合方法中使用非均相聚合催化剂。在一些实施例中，系统在聚合方法后不具有纯化系统。

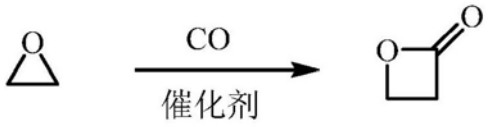
[0171] 在下文进一步详细描述丙烯酸和其前体的生产系统/生产方法中的每个单元操作。

[0172] β-丙内酯生产系统/生产方法(即羰基化反应系统)

[0173] 图14说明本文中所揭示的生产系统/生产方法的示范性实施例。图14含有羰基化反应系统1413(即β-丙内酯生产系统/生产方法)、催化剂隔离系统1415、BPL纯化系统1417、

聚合反应系统1419和热分解系统1421。

[0174] 在羰基化反应系统中，环氧乙烷可通过羰基化反应来转化成β-丙内酯，如以下反应流程中所描绘。

[0175] 

[0176] 水和氧可破坏羰基化催化剂。到羰基化反应系统的进料流(即EO、CO、溶剂、羰基化催化剂)实质上应为干燥的(即含水量低于5ppm)和不含氧的(即氧含量低于5ppm)。因此，进料流和/或储罐和/或进料罐可在其上具有传感器以便确定流/罐的组成，从而确保其具有足够低的含氧量和含水量。在一些实施例中，进料流可例如通过吸附来纯化以减少供应到羰基化反应系统的流中的含水量和氧含量。在一些实施例中，在运行生产系统/生产方法之前，导管、设备和其它流动路径可以用惰性气氛或一氧化碳吹扫，以使在生产系统/生产方法中暴露于氧或水降到最低。

[0177] 环氧乙烷源

[0178] 图14包含可以将环氧乙烷流1406中的新鲜环氧乙烷供应到羰基化反应系统入口1409的环氧乙烷源1402。入口1409可以是羰基化反应系统的一个入口或多个入口。可使用泵或所属领域一般技术人员已知的任何其它装置来将环氧乙烷作为液体供应。此外，环氧乙烷源可以维持在惰性氛围下。在一些实施例中，羰基化反应系统的入口可以至少约1000kg/hr、至少约1500kg/hr、至少约2000kg/hr、至少约2070kg/hr或至少约2500kg/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可以约1000kg/hr到约2500kg/hr、至少约1500kg/hr到约2500kg/hr、至少约2000kg/hr到约2500kg/hr或至少约2070kg/hr到约2500kg/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可以约1000kg/hr到约25000kg/hr、约1500kg/hr到约25000kg/hr、约2000kg/hr到约25000kg/hr、约2500kg/hr到约25000kg/hr、约5000kg/hr到约25000kg/hr、约7500kg/hr到约25000kg/hr、约10000kg/hr到约25000kg/hr、约12500kg/hr到约25000kg/hr、约15000kg/hr到约25000kg/hr、约17500kg/hr到约25000kg/hr、约20000kg/hr到约25000kg/hr或约22500kg/hr到约25000kg/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口到可以约1000kg/hr、约1500kg/hr、约2000kg/hr、约2070kg/hr、约2500kg/hr、约3000kg/hr、约3500kg/hr、约4000kg/hr、约4500kg/hr、约5000kg/hr、7500kg/hr、约10000kg/hr、约12500kg/hr、约15000kg/hr、约17500kg/hr、约20000kg/hr、约22500kg/hr或约25000kg/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可以至少约30kmol/hr、至少约35kmol/hr、至少约40kmol/hr、至少约47kmol/hr、至少约50kmol/hr、至少约100kmol/hr、至少约200kmol/hr、至少约300kmol/hr、至少约400kmol/hr或至少约500kmol/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可以约30kmol/hr到约500kmol/hr、约35kmol/hr到约500kmol/hr、约40kmol/hr到约500kmol/hr、约47kmol/hr到约500kmol/hr、约50kmol/hr到约500kmol/hr、约100kmol/hr到约500kmol/hr、约200kmol/hr到约500kmol/hr、约300kmol/hr到约500kmol/hr或约400kmol/hr到约500kmol/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可以约30kmol/hr、约35kmol/hr、约40kmol/hr、约47kmol/hr、约50kmol/hr、约70kmol/hr、

约80kmol/hr、约90kmol/hr、约100kmol/hr、约150kmol/hr、约200kmol/hr、约250kmol/hr、约300kmol/hr、约350kmol/hr、约400kmol/hr、约450kmol/hr或约500kmol/hr从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可在约10到30℃之间、约15到25℃之间或约20℃的温度下从环氧乙烷源接收环氧乙烷。在一些实施例中，羰基化反应系统的入口可在至少约50巴、约60到70巴或至少约65巴的压力下从环氧乙烷源接收环氧乙烷。

[0179] 羰基化催化剂源

[0180] 所属领域中已知的多种羰基化催化剂适合于(或可适于)本发明的方法。举例来说，在一些实施例中，羰基化方法使用金属羰基-路易斯酸催化剂(metal carbonyl-Lewis acid catalyst)，所述羰基化方法例如美国专利第6,852,865号中所描述的方法。在其它实施例中，羰基化步骤用揭示于美国专利申请序列第10/820,958号和第10/586,826号中的羰基化催化剂中的一或多种进行。在其它实施例中，羰基化步骤用揭示于美国专利案第5,310,948号、第7,420,064号和第5,359,081号中的催化剂中的一或多种进行。用于环氧化物的羰基化的额外催化剂在化学通讯(Chem.Commun.)，2007,657-674中的综述中讨论。前述参考文献中的每一篇的全部内容以引用的方式并入本文中。

[0181] 在一些实施例中，羰基化催化剂包含金属羰基化合物。通常，提供单一金属羰基化合物，但在一些实施例中，提供两种或多于两种金属羰基化合物的混合物。因此，当所提供的金属羰基化合物“包括”例如中性金属羰基化合物时，应理解所提供的金属羰基化合物可以是单一中性金属羰基化合物，或与一或多种金属羰基化合物组合的中性金属羰基化合物。优选地，所提供的金属羰基化合物能够使环氧化物开环并且促进CO插入到所得金属碳键中。具有此反应性的金属羰基化合物在所属领域中众所周知，并且用于实验室实验以及如氢甲酰化的工业工艺中。

[0182] 在一些实施例中，所提供的金属羰基化合物包括阴离子金属羰基部分。在其它实施例中，所提供的金属羰基化合物包括中性金属羰基化合物。在一些实施例中，所提供的金属羰基化合物包括金属羰基氢化物或氢化金属羰基化合物。在一些实施例中，所提供的金属羰基化合物充当预催化剂，其与一或多种反应组分就地反应以提供与最初提供的化合物不同的活性物种。专门涵盖此类预催化剂，因为应认识到，给出反应中的活性物种可能不能确定；因此就地鉴别此类反应性物种自身并不脱离本揭示的精神或教示内容。

[0183] 在一些实施例中，金属羰基化合物包括阴离子金属羰基物种。在一些实施例中，此类阴离子金属羰基物种具有通式$[Q_dM'_e(CO)_w]^{y-}$，其中Q是任何配位体并且不必存在，M'是金属原子，d是0到8的整数(包含端点)，e是1到6的整数(包含端点)，w是能够提供稳定的阴离子金属羰基络合物的数量并且y是阴离子金属羰基物种的电荷。在一些实施例中，阴离子金属羰基具有通式$[QM'(CO)_w]^{y-}$，其中Q是任何配位体并且不必存在，M'是金属原子，w是能够提供稳定的阴离子金属羰基的数量并且y是阴离子金属羰基的电荷。

[0184] 在一些实施例中，阴离子金属羰基物种包括周期表第5族、第7族或第9族的金属的单阴离子羰基络合物或周期表第4族或第8族的金属的双阴离子羰基络合物。在一些实施例中，阴离子金属羰基化合物含有钴或锰。在一些实施例中，阴离子金属羰基化合物含有铑。合适的阴离子金属羰基化合物包含但不限于：$[Co(CO)_4]^-$、$[Ti(CO)_6]^{2-}$、$[V(CO)_6]^-$、$[Rh(CO)_4]^-$、$[Fe(CO)_4]^{2-}$、$[Ru(CO)_4]^{2-}$、$[Os(CO)_4]^{2-}$、$[Cr_2(CO)_{10}]^{2-}$、$[Fe_2(CO)_8]^{2-}$、$[Tc(CO)_5]^-$、$[Re(CO)_5]^-$以及$[Mn(CO)_5]^-$。在一些实施例中，阴离子金属羰基包括$[Co(CO)_4]^-$。在一些实施

例中，两种或多于两种阴离子金属羰基络合物的混合物可存在于用于所述方法中的羰基化催化剂中。

[0185] 对于$[Q_dM'_e(CO)_w]^{y-}$的术语“能够提供稳定的阴离子金属羰基”在本文中用于意指$[Q_dM'_e(CO)_w]^{y-}$是可通过例如NMR、IR、X射线晶体学、拉曼光谱学(Raman spectroscopy)和/或电子自旋共振(EPR)的分析方法表征并且可在合适的阳离子或就地形成的物种存在下以催化剂形式分离的物种。应理解，可以形成稳定金属羰基络合物的金属具有已知的配位能力和倾向来形成多核络合物，与可能存在的任选配位体Q的数量和特征以及络合物上的电荷一起将决定可用于CO配位的位置数以及因此w的值。通常，此类化合物符合“18电子规则”。此类知识在关于金属羰基化合物的合成和表征的领域中的一般技术人员的掌握中。

[0186] 在所提供的金属羰基化合物是阴离子物种的实施例中，一或多个阳离子也必须存在。在一些变化形式中，对此类阳离子的特性无特定约束。在一些实施例中，与阴离子金属羰基化合物结合的阳离子包括本文中所描述的另一类别的反应组分。举例来说，在一些实施例中，金属羰基阴离子与阳离子路易斯酸结合。在其它实施例中与所提供的阴离子金属羰基化合物结合的阳离子是简单金属阳离子，例如来自周期表第1族或第2族的金属阳离子(例如Na^+、Li^+、K^+、Mg^{2+}等)。在其它实施例中，与所提供的阴离子金属羰基化合物结合的阳离子是庞大的非亲电阳离子，例如‘鎓盐’(例如Bu_4N^+、PPN^+、Ph_4P^+、Ph_4As^+等)。在其它实施例中，金属羰基阴离子与质子化氮化合物结合(例如阳离子可包括例如MeTBD-H^+、DMAP-H^+、DABCO-H^+、DBU-H^+等化合物)。在一些实施例中，包括此类质子化氮化合物的化合物提供为酸性氢化金属羰基化合物与碱性含氮化合物之间的反应产物(例如DBU和$HCo(CO)_4$的混合物)。

[0187] 在一些实施例中，用于本文中所描述的方法中的催化剂包括中性金属羰基化合物。在一些实施例中，此类中性金属羰基化合物具有通式$Q_dM'_e(CO)_{w'}$，其中Q是任何配位体并且不必存在，M’是金属原子，d是0到8的整数(包含端点)，e是1到6的整数(包含端点)并且w’是能够提供稳定的中性金属羰基络合物的数量。在一些实施例中，中性金属羰基具有通式$QM'(CO)_{w'}$。在一些实施例中，中性金属羰基具有通式$M'(CO)_{w'}$。在一些实施例中，中性金属羰基具有通式$QM'_2(CO)_{w'}$。在一些实施例中，中性金属羰基具有通式$M'_2(CO)_{w'}$。适合的中性金属羰基化合物包含但不限于：$Ti(CO)_7$、$V_2(CO)_{12}$、$Cr(CO)_6$、$Mo(CO)_6$、$W(CO)_6$、$Mn_2(CO)_{10}$、$Tc_2(CO)_{10}$和$Re_2(CO)_{10}$、$Fe(CO)_5$、$Ru(CO)_5$和$Os(CO)_5$、$Ru_3(CO)_{12}$和$Os_3(CO)_{12}$、$Fe_3(CO)_{12}$和$Fe_2(CO)_9$、$Co_4(CO)_{12}$、$Rh_4(CO)_{12}$、$Rh_6(CO)_{16}$和$Ir_4(CO)_{12}$、$Co_2(CO)_8$、$Ni(CO)_4$。

[0188] 对于$Q_dM'_e(CO)_{w'}$术语“以便提供稳定的中性金属羰基”在本文中用于意指$Q_dM'_e(CO)_{w'}$为可通过例如NMR、IR、X射线晶体学、拉曼光谱学和/或电子自旋共振(EPR)的分析方法表征并且可以纯形式分离的物种或就地形成的物种。应理解，可形成稳定金属羰基络合物的金属具有已知配位能力和倾向以形成多核络合物，与可存在的任选配体Q的数目和特征一起将决定可用于CO配位的位置数以及因此w’的值。通常，此类化合物符合符合“18-电子规则”的化学计量。此类知识在关于金属羰基化合物的合成和表征的领域中的一般技术人员的掌握中。

[0189] 在一些实施例中，没有配位体Q存在于金属羰基化合物上。在其它实施例中，一种或多种配体Q存在于金属羰基化合物上。在一些实施例中，其中存在Q，在每次出现时Q选自由以下组成的群组：膦配位体、胺配位体、环戊二烯基配位体、杂环配位体、腈、苯酚和这些

中的两个或两个以上的组合。在一些实施例中，上文所描述的金属羰基化合物中的任一个的CO配位体中的一或多个经配位体Q置换。在一些实施例中，Q是膦配位体。在一些实施例中，Q是三芳基膦。在一些实施例中，Q是三烷基膦。在一些实施例中，Q是亚磷酸酯配位体。在一些实施例中，Q是任选地经取代的环戊二烯基配位体。在一些实施例中，Q是cp。在一些实施例中，Q是cp*。Q是胺或杂环。

[0190] 在一些实施例中，用于上文所描述的方法中的羰基化催化剂进一步包含路易斯酸性组分。在一些实施例中，羰基化催化剂包括阴离子金属羰基络合物和阳离子路易斯酸组分。在一些实施例中，金属羰基络合物包含羰基钴酸盐并且路易斯酸性共催化剂包含以金属为中心的阳离子路易斯酸。在一些实施例中，所包含的路易斯酸包括硼化合物。

[0191] 在所包含的路易斯酸包括硼化合物的一些实施例中，硼化合物包括三烷基硼化合物或三芳基硼化合物。在一些实施例中，所包含的硼化合物包括一或多个硼-卤素键。在所包含的硼化合物包括一或多个硼-卤素键的一些实施例中，化合物是二烷基卤基硼化合物(例如R_2BX)、二卤基单烷基化合物(例如RBX_2)、芳基卤基硼化合物(例如Ar_2BX或$ArBX_2$)或三卤基硼化合物(例如BCl_3或BBr_3)，其中每个R是烷基；每个X是卤素；并且每个Ar是芳香族基团。

[0192] 在所包含的路易斯酸包括以为中心的阳离子路易斯酸的一些实施例中，路易斯酸是阳离子金属络合物。在一些实施例中，阳离子金属络合物具有其由一或多个阴离子金属羰基部分来部分或完全平衡的电荷。合适的阴离子金属羰基化合物包含上文所描述的阴离子金属羰基化合物。在一些实施例中，存在1到17个平衡金属络合物的电荷的此类阴离子金属羰基。在一些实施例中，存在1到9个平衡金属络合物的电荷的此类阴离子金属羰基。在一些实施例中，存在1到5个平衡金属络合物的电荷的此类阴离子金属羰基。在一些实施例中，存在1到3个平衡金属络合物的电荷的此类阴离子金属羰基。

[0193] 在用于本文中所描述的系统和方法中的羰基化催化剂包含阳离子金属络合物的一些实施例中，所述金属络合物具有式$[(L^c)_vM_b]^{z+}$，其中：

[0194] L^c是配位体，其中当存在两个或多于两个L^c时，每个可以相同或不同；

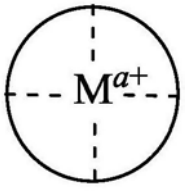
[0195] M是金属原子，其中当存在两个M时，每个可以相同或不同；

[0196] v是1到4的整数，包含端点；

[0197] b是1到2的整数，包含端点；并且

[0198] z是大于0的整数，代表金属络合物上的阳离子电荷。

[0199] 在一些实施例中，所提供的路易斯酸符合结构I：

[0200] 

I

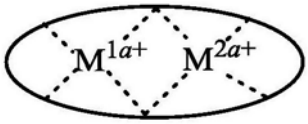
[0201] 其中：

[0202] 是多齿配位体；

[0203] M是与多齿配位体配位的金属原子；

[0204] a是金属原子的电荷并且在0到2范围内;并且

[0205] 在一些实施例中,所提供的金属络合物符合结构II:

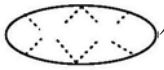
[0206] 

II

[0207] 其中a如上文所定义(每个a可以相同或不同),并且

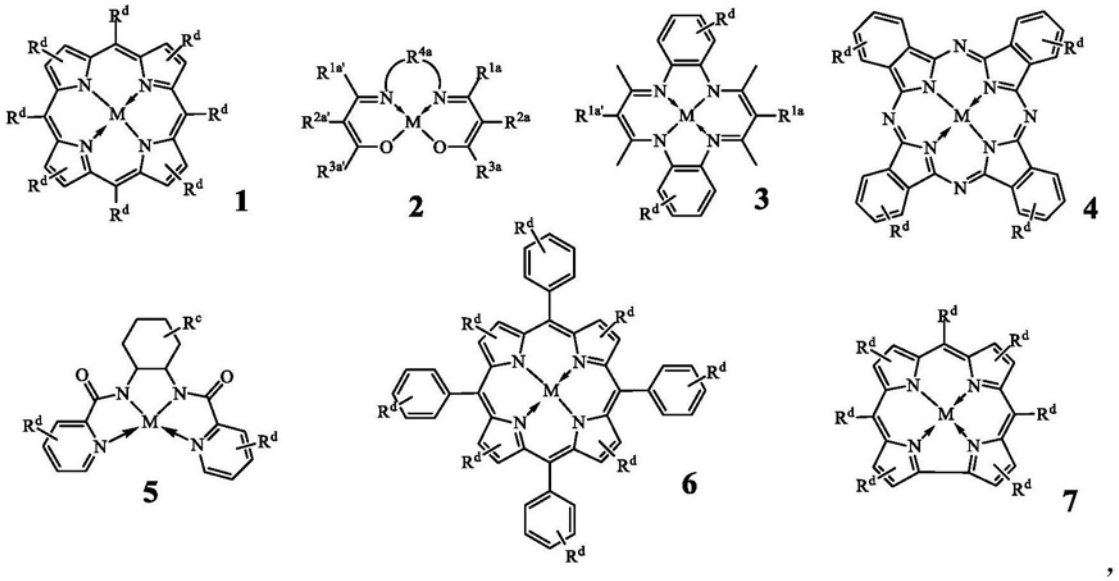
[0208] M^1是第一金属原子;

[0209] M^2是第二金属原子;

[0210] 包括能够配位两个金属原子的多齿配位体系统。

[0211] 为清楚起见,并且为避免混淆络合物I和II以及本文其它结构中的金属原子的净电荷和总电荷,以上络合物I和II中的金属原子上展示的电荷(a^+)表示在金属原子符合多齿配位体的任何阴离子位置之后所述金属原子上的净电荷。举例来说,如果式I络合物中的金属原子是Cr(III)并且配位体是卟啉(电荷是-2的四齿配位体),那么铬原子将具有+1净电荷并且a将是1。

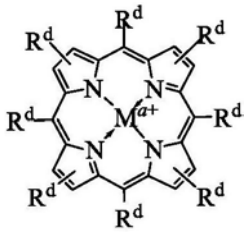
[0212] 适合的多齿配位体包含但不限于:卟啉衍生物1、沙仑衍生物2、二苯并四甲基四氮杂[14]轮烯(tmtaa)衍生物3、酞菁酸酯衍生物4、特罗斯特(Trost)配位体衍生物5、四苯基卟啉衍生物6以及咔咯衍生物7。在一些实施例中,多齿配位体是沙仑衍生物。在其它实施例中,多齿配位体是卟啉衍生物。在其它实施例中,多齿配位体是四苯基卟啉衍生物。在其它实施例中,多齿配位体是咔咯衍生物。

[0213] 

,

[0214] 其中R^c、R^d、R^a、R^{1a}、R^{2a}、R^{3a}、R^{4a}、$R^{1a'}$、$R^{2a'}$、$R^{3a'}$以及M中的每一个如本文中的类别和亚类中所定义和描述。

[0215] 在一些实施例中,用于本文中所描述的系统和方法中的羰基化催化剂所提供的路易斯酸包括金属卟啉络合物。在一些实施例中,部分具有结构:

[0216] 

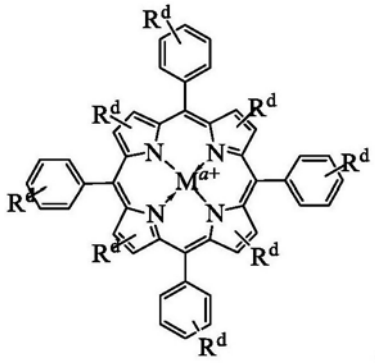
[0217] 其中M和a中的每一个如上文所定义且如本文中的类别和子类中所描述，并且

[0218] R^d在每次出现时独立地为氢、卤素、$-OR^4$、$-NR^y_2$、$-SR^y$、-CN、$-NO_2$、$-SO_2R^y$、$-SOR^y$、$-SO_2NR^y_2$、-CNO、$-NR^ySO_2R^y$、-NCO、$-N_3$、$-SiR^y_3$；或选自由以下组成的群组的任选地经取代基团：C_{1-20}脂肪族基；具有1到4个独立地选自由氮、氧和硫组成的群组的杂原子的C_{1-20}杂脂肪族基；6到10元芳基；具有1到4个独立地选自氮、氧和硫的杂原子的5到10元杂芳基；以及具有1到2个独立地选自由氮、氧和硫组成的群组的杂原子的4到7元杂环，其中两个或多于两个R^d基团可一起形成一或多个任选地经取代环，

[0219] 每个R^y独立地为氢、选自由以下组成的群组的任选经取代的基团：酰基；胺甲酰基、芳基烷基；6到10元芳基；C_{1-12}脂肪族基；具有1到2个独立地选自由氮、氧和硫组成的群组的杂原子的C_{1-12}杂脂肪族基；具有1到4个独立地选自由氮、氧或硫组成的群组的杂原子的5到10元杂芳基；具有1到2个独立地选自由氮、氧和硫组成的群组的杂原子的4到7元杂环；氧保护基；以及氮保护基；同一氮原子上的两个R^y与所述氮原子一起形成具有0到2个独立地选自由氮、氧和硫组成的群组的额外杂原子的任选地经取代的4到7元杂环；并且

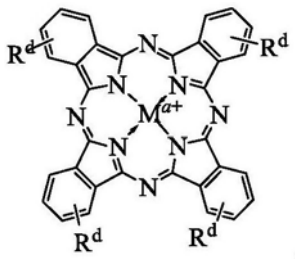
[0220] 每个R^4独立地为羟基保护基团或R^y。

[0221] 在一些实施例中，部分具有结构：

[0222] ，

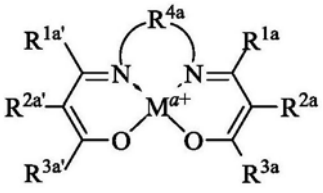
[0223] 其中M、a以及R^d如上文和本文中的类别和亚类中所定义。

[0224] 在一些实施例中，部分具有结构：

[0225] ，

[0226] 其中M、a以及R^d如上文和本文中的类别和亚类中所定义。

[0227] 在一些实施例中，包含在用于本文中所描述的系统和方法中的羰基化催化剂中的路易斯酸包括金属沙仑络合物。在一些实施例中，部分具有结构：

[0228] ，

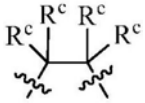
[0229] 其中：

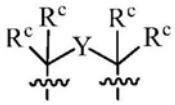
[0230] M、a以及R^d如上文和本文中的类别和亚类中所定义。

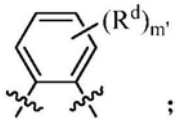
[0231] R^{1a}、$R^{1a'}$、R^{2a}、$R^{2a'}$、R^{3a}和$R^{3a'}$独立地为氢、卤素、$-OR^4$、$-NR^y_2$、$-SR^y$、-CN、$-NO_2$、$-SO_2R^y$、$-SOR^y$、$-SO_2NR^y_2$、-CNO、$-NR^ySO_2R^y$、-NCO、$-N_3$、$-SiR^y_3$；或选自由以下组成的群组的任选地经取代的基团：C_{1-20}脂肪族基、具有1到4个独立地选自由氮、氧和硫组成的群组的杂原子的C_{1-20}杂脂肪族基、6到10元芳基、具有1到4个独立地选自氮、氧和硫的杂原子的5到10元杂芳基；以及具有1到2个独立地选自由氮、氧和硫组成的群组的杂原子的4到7元杂环基；其中每个R^4和R^y独立地如上文所定义且如本文中的类别和子类中所描述，

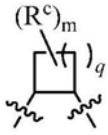
[0232] 其中($R^{2a'}$和$R^{3a'}$)、(R^{2a}和R^{3a})、(R^{1a}和R^{2a})和($R^{1a'}$和$R^{2a'}$)中的任一个可以任选地与其所连接的碳原子一起形成一或多个环，所述环又可以经一或多个R^y基团取代；并且

[0233] R^{4a}选自由以下组成的群组：

[0234] e) 

[0235] f) 

[0236] g)  和 ；

[0237] h)  其中 ，

[0238] R^c在每次出现时独立地为氢、卤素、$-OR^4$、$-NR^y_2$、$-SR^y$、-CN、$-NO_2$、$-SO_2R^y$、$-SOR^y$、$-SO_2NR^y_2$、-CNO、$-NR^ySO_2R^y$、-NCO、$-N_3$、$-SiR^y_3$；或选自由以下组成的群组的任选地经取代的基团：C_{1-20}脂肪族基；具有1到4个独立地选自由氮、氧和硫组成的群组的杂原子的C_{1-20}杂脂肪族基；6到10元芳基；具有1到4个独立地选自氮、氧和硫的杂原子的5到10元杂芳基；以及具有1到2个独立地选自由氮、氧和硫组成的群组的杂原子的4到7元杂环；

[0239] 其中：

[0240] 两个或多于两个R^c基团可以与其所连接的碳原子以及任何中间原子一起形成一或多个环；

[0241] 当两个R^c基团连接到同一碳原子时，其可以与其所连接的碳原子一起形成选自由

以下组成的群组的部分:3到8元螺环、羰基、肟、腙、亚胺以及任选地经取代的烯烃;

[0242] 其中R^4和R^y如上文和本文中的类别和子类中所定义;

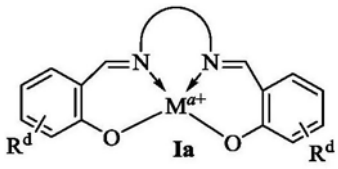
[0243] Y是选自由以下组成的群组的二价连接基团:-NR^y-、-N(R^y)C(O)-、-C(O)NR^y-、-O-、-C(O)-、-OC(O)-、-C(O)O-、-S-、-SO-、-SO_2-、-C(=S)-、-C(=NR^y)-、-N=N-;聚醚;C_3到C_8经取代或未经取代的碳环;以及C_1到C_8经取代或未经取代的杂环;

[0244] m'是0或1到4的整数,包含端点;

[0245] q是0或1到4的整数,包含端点;并且

[0246] x是0、1或2。

[0247] 在一些实施例中,所提供的路易斯酸包含金属沙仑化合物,如式Ia中所示:

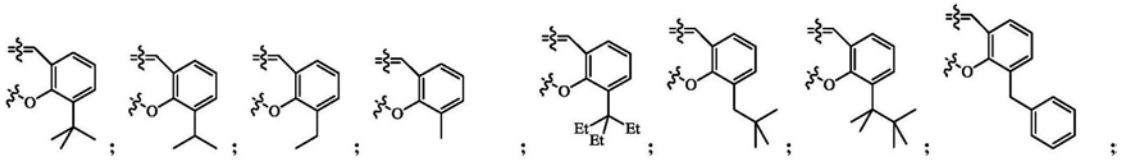
[0248] 

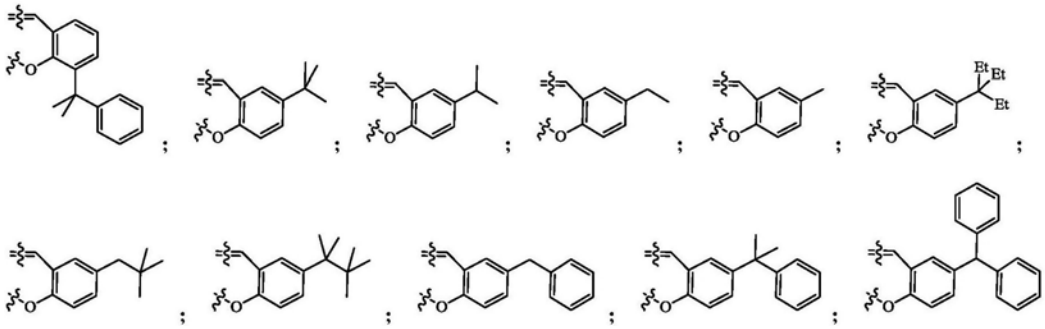
Ia ,

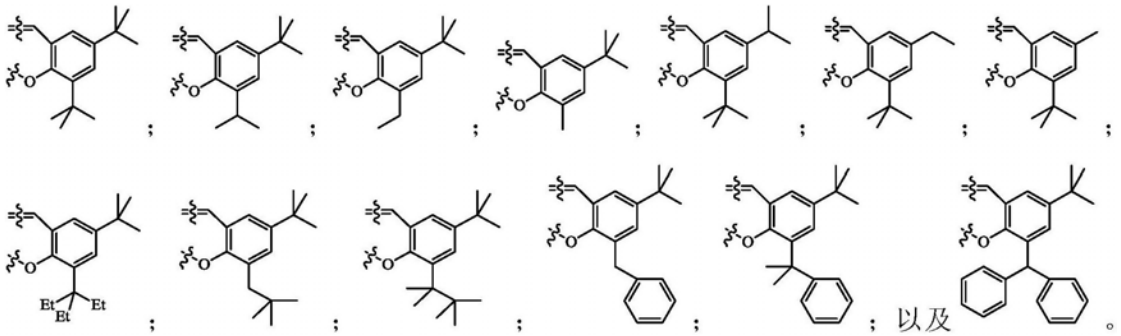
[0249] 其中M、R^d以及a中的每一个如上文和本文中的类别和子类中所定义,

[0250] 表示连接沙仑配位体的二胺部分的两个氮原子的任选地经取代的部分,其中选自由以下组成的群组:C_3到C_{14}碳环、C_6到C_{10}芳基、C_3到C_{14}杂环和C_5到C_{10}杂芳基;或任选地经取代的C_{2-20}脂肪族基团,其中一或多个亚甲基单元任选地且独立地经以下置换:-NR^y-、-N(R^y)C(O)-、-C(O)N(R^y)-、-OC(O)N(R^y)-、-N(R^y)C(O)O-、-OC(O)O-、-O-、-C(O)-、-OC(O)-、-C(O)O-、-S-、-SO-、-SO_2-、-C(=S)-、-C(=NR^y)-、-C(=NOR^y)-或-N=N-。

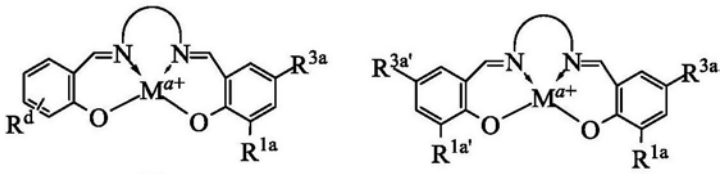
[0251] 在具有上文的式Ia的金属络合物的一些实施例中,包括金属络合物的水杨醛衍生部分的苯基环中的至少一个独立地选自由以下组成的群组:



[0252] 

[0253] 

[0254] 在一些实施例中，所提供的路易斯酸包含金属沙仑化合物，其符合式Va或Vb中的一个：

[0255] 

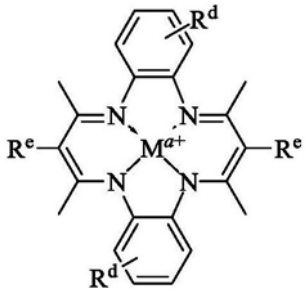
Va 或 Vb

[0256] 其中M、a、R^d、R^{1a}、R^{3a}、$R^{1a'}$、$R^{3a'}$和如上文和本文中的类别和亚类中所定义。

[0257] 在具有式Va或Vb的金属络合物的一些实施例中，每个R^{1a}和R^{3a}独立地为任选地经取代的C_1到C_{20}脂肪族基。

[0258] 在一些实施例中，部分包括任选地经取代的1,2-苯基部分。

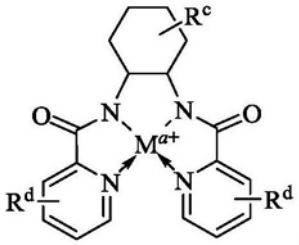
[0259] 在一些实施例中，包含在用于本文中所描述的系统和方法中的羰基化催化剂中的路易斯酸包括金属tmtaa络合物。在一些实施例中，部分具有结构：

[0260] 

[0261] 其中M、a以及R^d如上文和本文中的类别和亚类中所定义，且

[0262] R^e在每次出现时独立地为氢、卤素、-OR、-NR^y_2、-SR^y、-CN、-NO_2、-SO_2R^y、-SOR^y、-$SO_2NR^y_2$、-CNO、-$NR^ySO_2R^y$、-NCO、-N_3、-SiR^y_3；或选自由以下组成的群组的任选地经取代的基团：C_{1-20}脂肪族基；具有1到4个独立地选自由氮、氧和硫组成的群组的杂原子的C_{1-20}杂脂肪族基；6到10元芳基；具有1到4个独立地选自氮、氧和硫的杂原子的5到10元杂芳基；以及具有1到2个独立地选自由氮、氧和硫组成的群组的杂原子的4到7元杂环。

[0263] 在一些实施例中，部分具有结构：

[0264] 

[0265] 其中M、a、R^c和R^d中的每一个如上文和本文中的类别和亚类中所定义。

[0266] 在用于本文中所描述的系统和方法中的羰基化催化剂包含路易斯酸性金属络合物的一些实施例中，金属原子选自周期表第2到13族，包含端点。在一些实施例中，M是选自周期表第4、6、11、12和13族的过渡金属。在一些实施例中，M是铝、铬、钛、铟、镓、锌、钴或铜。在一些实施例中，M是铝。在其它实施例中，M是铬。

[0267] 在一些实施例中，M具有+2的氧化态。在一些实施例中，M是Zn(II)、Cu(II)、Mn(II)、Co(II)、Ru(II)、Fe(II)、Co(II)、Rh(II)、Ni(II)、Pd(II)或Mg(II)。在一些实施例中，M是Zn(II)。在一些实施例中，M是Cu(II)。

[0268] 在一些实施例中，M具有+3的氧化态。在一些实施例中，是Al(III)、Cr(III)、Fe(III)、Co(III)、Ti(III)、In(III)、Ga(III)或Mn(III)。在一些实施例中，M是Al(III)。在一些实施例中，M是Cr(III)。

[0269] 在一些实施例中，M具有+4的氧化态。在一些实施例中，M是Ti(IV)或Cr(IV)。

[0270] 在一些实施例中，M^1和M^2各独立地是选自周期表第2到13族(包含端点)的金属原子。在一些实施例中，M是选自周期表第4、6、11、12和13族的过渡金属。在一些实施例中，M是铝、铬、钛、铟、镓、锌、钴或铜。在一些实施例中，M是铝。在其它实施例中，M是铬。在一些实施例中，M^1和M^2相同。在一些实施例中，M^1和M^2是相同金属，但具有不同氧化态。在一些实施例中，M^1和M^2是不同金属。

[0271] 在一些实施例中，M^1和M^2中的一或多个具有+2的氧化态。在一些实施例中，M^1是Zn(II)、Cu(II)、Mn(II)、Co(II)、Ru(II)、Fe(II)、Co(II)、Rh(II)、Ni(II)、Pd(II)或Mg(II)。在一些实施例中，M^1是Zn(II)。在一些实施例中，M^1是Cu(II)。在一些实施例中，M^2是Zn(II)、Cu(II)、Mn(II)、Co(II)、Ru(II)、Fe(II)、Co(II)、Rh(II)、Ni(II)、Pd(II)或Mg(II)。在一些实施例中，M^2是Zn(II)。在一些实施例中，M^2是Cu(II)。

[0272] 在一些实施例中，M^1和M^2中的一或多个具有+3的氧化态。在一些实施例中，M^1是Al(III)、Cr(III)、Fe(III)、Co(III)、Ti(III)、In(III)、Ga(III)或Mn(III)。在一些实施例中，M^1是Al(III)。在一些实施例中，M^1是Cr(III)。在一些实施例中，M^2是Al(III)、Cr(III)、Fe(III)、Co(III)、Ti(III)、In(III)、Ga(III)或Mn(III)。在一些实施例中，M^2是Al(III)。在一些实施例中，M^2是Cr(III)。

[0273] 在一些实施例中，M^1和M^2中的一或多个具有+4的氧化态。在一些实施例中，M^1是Ti(IV)或Cr(IV)。在一些实施例中，M^2是Ti(IV)或Cr(IV)。

[0274] 在一些实施例中，羰基化催化剂中的以金属为中心的路易斯酸性组分包括双阴离子四齿配位体。在一些实施例中，双阴离子四齿配位体选自由以下组成的群组：卟啉衍生物；沙仑衍生物；二苯并四甲基四氮杂[14]轮烯(tmtaa)衍生物；酞菁酸酯衍生物；和特罗斯特配位体的衍生物。

[0275] 在一些实施例中，羰基化催化剂包含与铝卟啉化合物组合的羰基钴酸盐。在一些实施例中，羰基化催化剂是[(TPP)Al(THF)$_2$][Co(CO)$_4$]，其中TPP表示四苯基卟啉且THF表示四氢呋喃。

[0276] 在一些实施例中，羰基化催化剂包含与铬卟啉化合物组合的羰基钴酸盐。

[0277] 在一些实施例中，羰基化催化剂包含与铬沙仑化合物组合的羰基钴酸盐。在一些实施例中，羰基化催化剂包含与铬柳酰醋氨酚化合物组合的羰基钴酸盐。

[0278] 在一些实施例中，羰基化催化剂包含与铝沙仑化合物组合的羰基钴酸盐。在一些实施例中，羰基化催化剂包含与铝柳酰醋氨酚化合物组合的羰基钴酸盐。

[0279] 在一些实施例中，一或多个中性双电子供体与M、M^1或M^2配位并且填充金属原子的配位价。在一些实施例中，中性双电子供体是溶剂分子。在一些实施例中，中性双电子供体是醚。在一些实施例中，中性双电子供体是四氢呋喃、二乙醚、乙腈、二硫化碳或吡啶。在一些实施例中，中性双电子供体是四氢呋喃。在一些实施例中，中性双电子供体是环氧化物。在一些实施例中，中性双电子供体是酯或内酯。

[0280] 在某些实施例中，羰基化催化剂包含与铝卟啉化合物组合的羰基钴酸盐。在某些实施例中，羰基化催化剂包含与铬卟啉化合物组合的羰基钴酸盐。在某些实施例中，羰基化催化剂包含与铬沙仑化合物组合的羰基钴酸盐。在某些实施例中，羰基化催化剂包括与铬柳酰醋氨酚化合物组合的羰基钴酸盐。在某些实施例中，羰基化催化剂包含与铝沙仑化合物组合的羰基钴酸盐。在某些实施例中，羰基化催化剂包含与铝柳酰醋氨酚化合物组合的羰基钴酸盐。

[0281] 双相羰基化催化剂

[0282] 在一些实施例中，羰基化催化剂是双相的。因此，在某些变化形式中，羰基化反应产物混合物包括至少两种相，其中一种相是催化剂相且第二相是产物相，其中在羰基化反应之后，大部分羰基化催化剂位于催化剂相，且所生产的大部分bPL位于产物相。举例来说，在一些实施例中，介于50wt％与100wt％之间、介于60wt％与100wt％之间、介于70wt％与100wt％之间、介于80wt％与100wt％之间、介于90wt％与100wt％之间或介于95wt％与100wt％之间的羰基化催化剂位于催化剂相。在一些实施例中，所产生的介于50wt％与100wt％之间、介于60wt％与100wt％之间、介于70wt％与100wt％之间、介于80wt％与100wt％之间、介于90wt％与100wt％之间或介于95wt％与100wt％之间的bPL位于位于产物相。在一些实施例中，双相羰基化催化剂是本文中所描述的羰基化催化剂中的任一种，限制条件为催化剂至少部分地不可与bPL混溶。在其它实施例中，羰基化催化剂是本文中所描述的经修改以含有取代基从而使经修改的催化剂至少部分地不可与bPL混溶的羰基化催化剂中的任一种。

[0283] 在一些实施例中，羰基化催化剂在某些条件下至少部分地不可与bPL混溶，但在其它条件下可与bPL混溶。举例来说，在一些变化形式中双相催化剂在一个温度下可与羰基化产物流中的bPL完全混溶，且在更低温度下至少部分地不可与羰基化产物流中的bPL混溶。在其它变化形式中双相催化剂包括一或多个可电离官能团，其使得催化剂在一个pH下可与羰基化产物流中的bPL混溶，且在另一pH下至少部分地不可混溶。因此，在一些实施例中，双相催化剂在第一pH下与EO和CO组合以产生bPL，其中所述催化剂可与bPL混溶，且随后反应混合物的pH改变以使得双相催化剂至少部分地不可与bPL混溶。

[0284] 监测和置换催化剂

[0285] 在一个方面中,生产系统/生产方法被配置成用于连续羰基化环氧化物或内酯原料,所述方法包括以下步骤:

[0286] 在催化剂存在下使环氧化物或内酯原料与一氧化碳反应,所述催化剂包括路易斯酸和羰基化反应容器中的金属羰基;

[0287] 测量一或多个选自由以下组成的群组的参数:

[0288] i)路易斯酸或其分解产物在羰基化反应容器内的浓度;

[0289] ii)路易斯酸或其分解产物在来自羰基化反应容器的产物流下游中的浓度;

[0290] iii)金属羰基或其分解产物在羰基化反应容器内的浓度;

[0291] iv)金属羰基或其分解产物在来自羰基化反应容器的产物流下游中的浓度;以及

[0292] v)羰基化反应的速率;

[0293] 将一或多个参数的测量值与一或多个参数的预定参考值进行比较;且

[0294] 其中参数中的任一个的测量值i)、iii)或v)小于参考值,或其中参数中的任一个的测量值ii)或iv)大于参考值,从而将催化剂替换组分引入到羰基化反应容器,所述催化剂替换组分不同于催化剂且包括选自由以下组成的群组的物种:路易斯酸、路易斯酸的前体、金属羰基以及金属羰基的前体。

[0295] 在一些实施例中,所测量的一或多个参数中的一个是路易斯酸或其分解产物在羰基化反应容器内的浓度。在一些实施例中,测量路易斯酸在羰基化反应容器内的浓度。在一些实施例中,测量路易斯酸的分解产物在羰基化反应容器内的浓度。

[0296] 在一些实施例中,所测量的一或多个参数中的一个是金属羰基或其分解产物在羰基化反应容器内的浓度。在一些实施例中,测量金属羰基在羰基化反应容器内的浓度。在一些实施例中,测量金属羰基的分解产物在羰基化反应容器内的浓度。

[0297] 在一些实施例中,所测量的一或多个参数中的一个是路易斯酸或其分解产物在来自羰基化反应容器的产物流下游中的浓度。在一些实施例中,测量路易斯酸在来自羰基化反应容器的产物流下游中的浓度。在一些实施例中,测量路易斯酸的分解产物在来自羰基化反应容器的产物流下游中的浓度。

[0298] 在一些实施例中,所测量的一或多个参数中的一个是金属羰基或其分解产物在来自羰基化反应容器的产物流下游中的浓度。在一些实施例中,测量金属羰基在来自羰基化反应容器的产物流下游中的浓度。在一些实施例中,测量金属羰基的分解产物在来自羰基化反应容器的产物流下游中的浓度。

[0299] 在一些实施例中,所测量的一或多个参数中的一个是羰基化反应的速率。在一些实施例中,羰基化反应的速率通过随时间推移羰基化产物在羰基化反应容器中的浓度变化来测量。在一些实施例中,羰基化反应的速率通过随时间推移羰基化产物在来自羰基化反应容器的产物流下游中的浓度变化来测量。在一些实施例中,羰基化产物是β-丙内酯。在一些实施例中,羰基化产物是β-丙内酯(bPL)。在一些实施例中,羰基化产物是丁二酸酐。在一些实施例中,羰基化产物是丁二酸酐(SA)。

[0300] 在一些实施例中,产物流通过纳滤膜从羰基化反应器中分离。在一些实施例中,纳滤膜基于其能够保留溶质而选择,所述溶质的分子量大于环氧化物或内酯羰基化产物的分子量但小于路易斯酸或金属羰基的分子量。在一些实施例中,纳滤膜被设计成保留溶质,所

述溶质的分子量大于环氧化物或内酯羰基化产物的分子量但小于路易斯酸或金属羰基的分子量。

[0301] 在一些实施例中，催化剂替代组分包括路易斯酸或路易斯酸的前体。在一些实施例中，催化剂替代组分包括路易斯酸。在一些实施例中，催化剂替代组分包括路易斯酸的前体。

[0302] 在一些实施例中，催化剂替代组分包括金属羰基或金属羰基的前体。在一些实施例中，催化剂替代组分包括金属羰基。在一些实施例中，催化剂替代组分包括金属羰基的前体。

[0303] 在一些实施例中，当添加多于一种催化剂替代组分时，一或多种催化剂替代组分中的每一种单独地添加到羰基化反应器。在一些实施例中，当添加多于一种催化剂替代组分时，全部一或多种催化剂替代组分一起添加到羰基化反应器。

[0304] 在一些实施例中，一或多种催化剂替代组分中的每一种作为于有机溶剂中的溶液或作为研磨浆在没有溶剂的情况下单独地添加到羰基化反应器。在一些实施例中，一或多种催化剂替代组分中的每一种在没有溶剂的情况下添加到羰基化反应器。在一些实施例中，一或多种催化剂替代组分中的每一种作为于有机溶剂中的溶液添加到羰基化反应器。在一些实施例中，一或多种催化剂替代组分中的每一种作为研磨浆添加到羰基化反应器。

[0305] 在某些实施例中，当添加多于一种催化剂替代组分时，每种催化剂替代组分溶解于溶液中，且溶液例如通过使用混合三通或使组合的溶液流动穿过静态混合器来在到容器的途中组合。

[0306] 在某些实施例中，新鲜催化剂还可在与一或多种催化剂替代组分相同或不同的时间时添加到反应器。

[0307] 在某些实施例中，催化剂替代组分在包括CO的氛围下添加。在某些实施例中，CO存在于约1个大气压到约400个大气压的压力下。在某些实施例中，催化剂替代组分在约1个大气压与约100个大气压之间、或约1个大气压与约50个大气压之间、或约10个大气压与约20个大气压之间、或约5个大气压与约10个大气压之间、或约1个大气压与约5个大气压之间的压力下在包括CO的氛围下添加。

[0308] 在一些实施例中，添加到羰基化反应器的给定催化剂替代组分的量与步骤(a)中所测量的参数中的一个成比例。在一些实施例中，给定催化剂替代组分的量与羰基化反应器下游的产物流中所测量的参数的浓度中的变化成正比。

[0309] 在一些实施例中，如果步骤(a)中所测量的羰基化反应器下游的产物流中的路易斯酸或其分解产物的浓度增加，那么与步骤(a)中所测量的路易斯酸或其分解产物的浓度中的增加成正比的量的路易斯酸添加到羰基化反应器。在一些实施例中，如果步骤(a)中所测量的羰基化反应器内的路易斯酸或其分解产物的浓度降低，那么与步骤(a)中所测量的路易斯酸或其分解产物的浓度中的降低成正比的量的路易斯酸或路易斯酸的前体添加到羰基化反应器。举例来说，如果路易斯酸的浓度已降低5％，那么添加等效于约5％的量的最初填充到羰基化反应器中的路易斯酸的量的路易斯酸或路易斯酸的前体。

[0310] 在一些实施例中，如果步骤(a)中所测量的羰基化反应的速率降低，那么与羰基化反应的速率中的降低成正比的量的路易斯酸或路易斯酸的前体添加到羰基化反应器。在一些实施例中，如果步骤(a)中所测量的羰基化反应的速率降低，那么与羰基化反应的速率中

的降低成正比的量的金属羰基或金属羰基的前体添加到羰基化反应器。举例来说，如果羰基化反应的速率已降低5％，那么添加等效于约5％的量的最初填充到羰基化反应器中的路易斯酸或金属羰基的量的路易斯酸、路易斯酸的前体、金属羰基或金属羰基的前体。

[0311] 在一些实施例中，如果步骤(a)中所测量的羰基化反应器的产物流下游中的金属羰基的浓度增加，那么与步骤(a)中所测量的金属羰基的量中的增加成正比的量的金属羰基或金属羰基的前体添加到羰基化反应器。在一些实施例中，如果步骤(a)中所测量的羰基化反应器内的金属羰基或其分解产物的浓度降低，那么与步骤(a)中所测量的金属羰基或其分解产物的量中的降低成正比的量的金属羰基或金属羰基的前体添加到羰基化反应器。举例来说，如果金属羰基的浓度已降低5％，那么添加等效于约5％的量的最初填充到羰基化反应器中的金属羰基的量的金属羰基或金属羰基的前体。

[0312] 图14包含羰基化催化剂源1403，其可将羰基化催化剂流1407中的新鲜羰基化催化剂供应到羰基化反应系统入口1409。羰基化催化剂可呈固体(可能覆盖在CO或合适的惰性气体下)或在如己烷或THF的溶剂的溶液中到达羰基化催化剂源。如果为固体催化剂，那么固体可在惰性条件(例如，CO或惰性气体)下解封装且装入一或多个料斗中。来自一或多个料斗的固体可在泵送之前计量加入合适的溶剂。在一些实施例中，固体催化剂(或液体催化剂)或催化剂前体可从运送容器(vessel/container)分配到中间惰性容器中以与溶剂混合且随后泵送。在一些实施例中，选择催化剂制备系统和连接件以使得催化剂/前体不暴露于大气压。羰基化催化剂溶液可适合于直接泵送到羰基化反应系统。在一些实施例中，羰基化催化剂进料在CO压力下泵送以帮助确保催化剂的稳定性。此外，羰基化催化剂源和进料可冷却到低于环境温度以确保稳定性。在一些实施例中，羰基化反应系统的入口可以约0.01到50kg/hr之间、约0.01到40kg/hr之间、约0.01到30kg/hr之间、约0.01到20kg/hr之间、约0.01到10kg/hr之间、约0.2到5kg/hr之间、约0.5到4kg/hr之间、约1到3kg/hr之间、约1到2kg/hr之间、或约1.4kg/hr接收来自羰基化催化剂源的羰基化催化剂。在一些实施例中，羰基化反应系统的入口可以约0.0001到10kmol/hr之间、约0.0001到1kmol/hr之间、约0.0001到0.1kmol/hr之间、约0.0001到0.01kmol/hr之间、约0.0005到0.001kmol/hr之间、约0.0005到0.005kmol/hr之间、或约0.001kmol/hr、或约0.01kmol/hr、或约0.1kmol/hr接收来自羰基化催化剂源的羰基化催化剂。在一些实施例中，羰基化催化剂可在如THF的溶剂中，以使得羰基化催化剂源的流中的羰基化催化剂的质量分数可在约0.001到0.1、约0.005到0.05、约0.01到0.05之间或约0.02。在一些实施例中，羰基化反应系统入口可在约10到30℃之间、约15到25℃之间、或约20℃的温度下接收来自羰基化催化剂源的羰基化催化剂。在一些实施例中，羰基化反应系统的入口可在至少约50巴、约60到70巴、或至少约65巴的压力下接收来自羰基化催化剂源的羰基化催化剂。

[0313] 一氧化碳源

[0314] 一氧化碳以足以使环氧乙烷羰基化来产生β-丙内酯的量供应到β-丙内酯生产系统/生产方法中。在一些变化形式中，这可在超大气压力的一氧化碳下进行羰基化反应来实现。在某些实施例中，一氧化碳在约50psi(350kPa)到约5000psi(35MPa)的范围内的压力下提供到β-丙内酯生产系统/生产方法中。在某些实施例中，一氧化碳在约50psi(350kPa)到约1000psi(7MPa)的压力下提供到β-丙内酯生产系统/生产方法中。在某些实施例中，一氧化碳在约50psi(350kPa)到约500psi(3.5MPa)的压力下提供到β-丙内酯生产系统/生产方

法中。在某些实施例中，一氧化碳在约100psi(700kPa)到约400psi(2.8MPa)的压力下提供到β-丙内酯生产系统/生产方法中。在某些实施例中，一氧化碳在约200psi(1.4MPa)的压力下提供到β-丙内酯生产系统/生产方法中。在某些实施例中，一氧化碳在具有约200psi(1.4MPa)CO的分压的氛围下提供到β-丙内酯生产系统/生产方法中。超大气压力的一氧化碳可以纯一氧化碳形式提供，或通过提供含有一氧化碳的气体混合物来提供。在某些实施例中，一氧化碳可以大体上纯一氧化碳的形式提供。在其它实施例中，一氧化碳可以一氧化碳与一或多种惰性气体的混合物形式提供。在其它实施例中，一氧化碳可以一氧化碳与氢的混合物形式提供。在某些实施例中，一氧化碳可以含有一氧化碳的工业过程气体(如合成气、煤气、木炭气等)形式提供。

[0315] 图14包含一氧化碳源1411，其可将一氧化碳供应到羰基化反应系统入口1409。在一些实施例中，将一氧化碳供应到羰基化反应系统的一氧化碳源可包含新鲜一氧化碳源1401(即，主要CO进料)和来自羰基化反应系统的再循环一氧化碳流1410。在一些实施例中，一氧化碳源可仅为新鲜一氧化碳源。在一些实施例中，一氧化碳源可仅为再循环一氧化碳。在一些实施例中，新鲜一氧化碳流1405和/或再循环一氧化碳流可在来自一氧化碳压缩机的所得流(即，反应器一氧化碳入口流)供应到羰基化反应系统中之前供应到一氧化碳压缩机1401A中。在一些实施例中，来自一氧化碳压缩机1411的所得流(即，反应系统一氧化碳入口流)可为一氧化碳源。一氧化碳源可压缩到羰基化反应系统压力的压力或高于所述羰基化反应系统压力的压力，且随后供应到羰基化系统。在一些实施例中，新鲜一氧化碳源(即，主要CO进料)和再循环一氧化碳可在单独压缩机中压缩。再循环一氧化碳单独地从新鲜一氧化碳进料(即，主要CO进料)压缩到反应系统压力的一个原因为避免有害组分污染主压缩机(即，新鲜进料压缩机)，所述有害组分如可存在于一氧化碳再循环流中的环氧乙烷和bPL。这些潜在地有害组分中的一些可随着将组分部分液化为废液而从压缩机中移除。在一些实施例中，这些潜在地有害组分也可再循环到羰基化反应系统。在一些实施例中，来自两个压缩机的压缩的一氧化碳可作为反应系统一氧化碳入口流供应到羰基化反应系统。

[0316] 在一些实施例中，新鲜一氧化碳源可提供至少约1000kg/hr CO、至少约1200kg/hr CO、至少约1400kg/hr CO、至少约1500kg/hr CO、至少约1600kg/hr CO、至少约2000kg/hr CO、至少约4000kg/hr CO、至少约5000kg/hr CO、至少约10000kg/hr CO、至少约12000kg/hr CO、至少约14000kg/hr CO、至少约15000kg/hr CO、或至少约16000kg/hr CO。在一些实施例中，新鲜一氧化碳源可提供至少约30kmol/hr CO、至少约40kmol/hr CO、至少约50kmol/hr CO、至少约55kmol/hr CO、或至少约60kg/hr CO。在一些实施例中，新鲜一氧化碳源可提供约1000kg/hr CO到约16000kg/hr CO、约1200kg/hr CO到约16000kg/hr CO、约1400kg/hr CO到约16000kg/hr CO、约1500kg/hr CO到约16000kg/hr CO、约1600kg/hr CO到约16000kg/hr CO、约2000kg/hr CO到约16000kg/hr CO、约4000kg/hr CO到约16000kg/hr CO、约6000kg/hr CO到约16000kg/hr CO、约1000kg/hr CO到约16000kg/hr CO、或约1400kg/hr CO到约16000kg/hr CO。在一些实施例中，新鲜一氧化碳源可提供约1000kg/hr CO、约1200kg/hr CO、约1400kg/hr CO、约1500kg/hr CO、约1600kg/hr CO、约1800kg/hr CO、约2000kg/hr CO、约2400kg/hr CO、约2600kg/hr CO、约2800kg/hr CO、约3000kg/hr CO、约3200kg/hr CO、约4000kg/hr CO、约6000kg/hr CO、约8000kg/hr CO、约10000kg/hr CO、约12000kg/hr CO、约14000kg/hr CO、或约16000kg/hr CO。在一些实施例中，新鲜一氧

化碳源可提供至少约30kmol/hr CO、至少约40kmol/hr CO、至少约50kmol/hr CO、至少约55kmol/hr CO、至少约60kmol/hr CO、至少约100kmol/hr CO、至少约150kmol/hr CO、至少约200kmol/hr CO、至少约250kmol/hr CO、至少约300kg/hr CO、至少约350kmol/hr CO、至少约400kmol/hr CO、至少约500kmol/hr CO、至少约550kmol/hr CO、或至少约600kg/hr CO。在一些实施例中，新鲜一氧化碳源可提供约30kmol/hr CO到约60kmol/hr CO、约40kmol/hr CO到约60kmol/hr CO、约50kmol/hr CO到约60kmol/hr CO、约30kmol/hr CO到约600kmol/hr CO、约40kmol/hr CO到约600kmol/hr CO、约50kmol/hr CO到约600kmol/hr CO、约55kmol/hr CO到约600kmol/hr CO、约100kmol/hr CO到约600kmol/hr CO、约200kg/hr CO到约600kmol/hr CO、约300kmol/hr CO到约600kmol/hr CO、约400kmol/hr CO到约600kmol/hr CO、约500kmol/hr CO到约600kmol/hr CO、约525kmol/hr CO到约600kmol/hr CO、约550kg/hr CO到约600kmol/hr CO。在一些实施例中，来自新鲜一氧化碳源的新鲜一氧化碳可具有一些杂质且由此可需要如吸附的额外纯化步骤。在一些实施例中，新鲜一氧化碳源的流动速率设定为约为羰基化反应的化学计量值、设定为比化学计量值高约5％、设定为比化学计量值高约10％、设定为比化学计量值高约15％、或比化学计量值高约20％。

[0317] 在一些实施例中，来自羰基化反应系统的再循环一氧化碳可提供至少约100kg/hr CO、至少约150kg/hr CO、至少约200kg/hr CO、至少约255kg/hr CO、至少约300kg/hr CO、至少约350kg/hr CO、至少约500kg/hr CO、至少约600kg/hr CO、至少约800kg/hr CO、至少约1000kg/hr CO、至少约1250kg/hr CO、至少约1500kg/hr CO、至少约1750kg/hr CO、至少约2000kg/hr CO、至少约2500kg/hr CO、至少约3000kg/hr CO、或至少约3500kg/hr CO。在一些实施例中，来自羰基化反应系统的再循环一氧化碳可提供约100kg/hr CO到约350kg/hr CO、约150kg/hr CO到约350kg/hr CO、约200kg/hr CO到约350kg/hr CO、约255kg/hr CO到约350kg/hr CO、约300kg/hr CO到约350kg/hr CO、约100kg/hr CO到约3500kg/hr CO、约150kg/hr CO到约3500kg/hr CO、约200kg/hr CO到约3500kg/hr CO、约255kg/hr CO到约3500kg/hr CO、约300kg/hr CO到约3500kg/hr CO、约350kg/hr CO到约3500kg/hr CO、约1000kg/hr CO到约3500kg/hr CO、约1500kg/hr CO到约3500kg/hr CO、约2000kg/hr CO到约3500kg/hr CO、约2550kg/hr CO到约3500kg/hr CO、约3000kg/hr CO到约3500kg/hr CO。在一些实施例中，来自羰基化反应系统的再循环一氧化碳可提供约100kg/hr CO、约150kg/hr CO、约200kg/hr CO、约255kg/hr CO、约300kg/hr CO、约350kg/hr CO、约500kg/hr CO、约750kg/hr CO、约1000kg/hr CO、约1250kg/hr CO、约1500kg/hr CO、约2000kg/hr CO、约2500kg/hr CO、约3000kg/hr CO、或约3500kg/hr CO。在一些实施例中，再循环一氧化碳源可提供至少约3kmol/hr CO、至少约5kmol/hr CO、至少约7kmol/hr CO、至少约9kmol/hr CO、至少约10kmol/hr CO、至少约15kmol/hr CO、至少50kmol/hr CO、至少100kmol/hr CO、或至少150kmol/hr CO。在一些实施例中，再循环一氧化碳流中的CO的质量分数可为至少约0.70、至少约0.75、至少约0.8、或至少约0.85。在一些实施例中，再循环一氧化碳流中的CO的摩尔分数可为至少约0.70、至少约0.75、至少约0.8、至少约0.85、至少约0.896、至少约0.9、或至少约0.95。在一些实施例中，再循环一氧化碳流中的CO的摩尔分数可为0.70到1.0、0.75到1.0、0.8到1.0、0.85到1.0、0.896到1.0、0.9到1.0、或0.95到1.0。来自羰基化反应系统的再循环一氧化碳流也可包含：不反应的环氧乙烷(呈约至多10kg/hr、至多15kg/hr、至多20kg/hr、至多25kg/hr、至多50kg/hr、至多75kg/hr、至多100kg/hr、至多150kg/hr、

至多200kg/hr、或至多250kg/hr，或呈约0.05到0.075、约0.055到0.07、约0.06到0.07、约至多0.065、约至多0.07、或约至多0.075之间的质量分数)，副反应产物乙醛(呈约至多0.5kg/hr、至多约1kg/hr、至多约1.3kg/hr、至多约2kg/hr、至多约4kg/hr、至多约6kg/hr、至多约10kg/hr、至多约13kg/hr，或呈约0.001到0.009、约0.003到0.005、或约至多0.004、约至多0.005、或至多约0.009的质量分数)，bPL(呈至多约0.005kg/hr、至多约0.01kg/hr、至多约0.015kg/hr、至多约0.019kg/hr、至多约0.05kg/hr、至多约0.1kg/hr、至多约0.15kg/hr、或至多约0.19kg/hr)，以及剩余溶剂(例如，THF)。

[0318] 在一些实施例中，羰基化反应系统的入口可以至少约1000kg/hr、至少约1250kg/hr、至少约1500kg/hr、至少约1600kg/hr、至少约1655kg/hr、至少约1700kg/hr、至少约4000kg/hr、至少约5000kg/hr、至少约700kg/hr、至少约8500kg/hr、至少约10000kg/hr、至少约12500kg/hr、至少约15000kg/hr、至少约16000kg/hr、至少约16550kg/hr、或至少约17000kg/hr接收来自一氧化碳源的一氧化碳。在一些实施例中，羰基化反应系统的入口可以约1000kg/hr到约1700kg/hr、约1250kg/hr到约1700kg/hr、约1500kg/hr到约1700kg/hr、约1600kg/hr到约1700kg/hr、约1655kg/hr到约1700kg/hr、1000kg/hr到约17000kg/hr、约1250kg/hr到约17000kg/hr、约1500kg/hr到约17000kg/hr、约1600kg/hr到约17000kg/hr、约1655kg/hr到约17000kg/hr、约1700kg/hr到约17000kg/hr、以约2000kg/hr到约17000kg/hr、约3000kg/hr到约17000kg/hr、约4000kg/hr到约17000kg/hr、约6000kg/hr到约17000kg/hr、约8000kg/hr到约17000kg/hr、约1200kg/hr到约17000kg/hr、约1400kg/hr到约17000kg/hr、约1500kg/hr到约17000kg/hr、或约1600kg/hr到约17000kg/hr接收来自一氧化碳源的一氧化碳。在一些实施例中，羰基化反应系统的入口可以约1000kg/hr、约1250kg/hr、约1500kg/hr、约1600kg/hr、约1655kg/hr、约1700kg/hr、约2000kg/hr、约1900kg/hr、约2500kg/hr、约3000kg/hr、约4000kg/hr、约6000kg/hr、约8000kg/hr、约10000kg/hr、约12000kg/hr、约13000kg/hr、约14000kg/hr、约15000kg/hr、约16000kg/hr、或约17000kg/hr接收来自一氧化碳源的一氧化碳。在一些实施例中，羰基化反应系统的入口可以至少约35kmol/hr、至少约45kmol/hr、至少约50kmol/hr、至少约55kmol/hr、或至少约59kmol/hr接收来自一氧化碳源的一氧化碳。如先前论述，在一些实施例中，一氧化碳源可包含来自羰基化反应系统的一些再循环一氧化碳。因此，在一些实施例中，羰基化反应系统的入口也可接收：环氧乙烷(呈约5到300kg/hr、约10到200kg/hr、约10到100kg/hr、约10到50kg/hr、约10到30kg/hr、约10到20kg/hr、或至多约15kg/hr、至多约50kg/hr、至多约100kg/hr、至多约150kg/hr、至多约200kg/hr、至多约300kg/hr，或呈约0.001到0.05、约0.005到0.02、或至多约0.009、至多约0.02、或至多约0.05的质量分数)，乙醛(呈约0.25到15kg/hr、约0.5到12.5kg/hr、约0.25到10kg/hr、约0.5到5kg/hr、约0.25到1.5kg/hr、约0.5到1.25kg/hr、或至多约0.9kg/hr、至多约1.5kg/hr、至多约3kg/hr、至多约6kg/hr、至多约12kg/hr、至多约15kg/hr，或呈约0.001到0.05、约0.005到0.02、或至多约0.009、至多约0.02、或至多约0.05的质量分数)，以及来自一氧化碳源的剩余溶剂。在一些实施例中，来自一氧化碳源的CO的质量分数可为至少约0.9、至少约0.95、至少约0.985、或至少约0.99。在一些实施例中，来自一氧化碳源的CO的摩尔分数可为至少约0.9、至少约0.95、至少约0.98、至少约0.99、或至少约0.995。在一些实施例中，来自一氧化碳源的CO的摩尔分数可为0.9到1.0、0.95到1.0、0.98到1.0、0.99到1.0、或0.995到1.0。

[0319] 在一些实施例中，羰基化反应系统的入口可自一氧化碳源接收在约10到170℃之间、约30到70℃之间、约40到60℃之间、约45到55℃之间、或约50℃的温度下的一氧化碳。在一些实施例中，羰基化反应系统的入口可自一氧化碳源接收在至少约50巴、约60到70巴、或至少约65巴的压力下的一氧化碳。

[0320] 溶剂源

[0321] 溶剂可选自本文中所描述的任何溶剂和这类溶剂的混合物。在一些变化形式中，溶剂为有机溶剂。在某些变化形式中，溶剂为非质子溶剂。

[0322] 在一些实施例中，溶剂包含二甲基甲酰胺、N-甲基吡咯烷酮、四氢呋喃、甲苯、二甲苯、二乙醚、甲基叔丁基醚、丙酮、甲基乙基酮、甲基异丁基酮、乙酸丁酯、乙酸乙酯、二氯甲烷和己烷以及这些溶剂中的任何两种或大于两种的混合物。一般而言，极性非质子溶剂或烃适合于这一步骤。

[0323] 另外，在一种变化形式中，β-内酯可用作共溶剂。在其它变化形式中，溶剂可包含醚、烃和非质子极性溶剂。在一些实施例中，溶剂包含四氢呋喃(“THF”)、环丁砜、N-甲基吡咯烷酮、1,3二甲基-2-咪唑啉酮、二乙二醇二甲醚、三乙二醇二甲醚、四乙二醇二甲醚、二乙二醇二丁醚、异山梨醇醚、甲基叔丁基醚、二乙醚、二苯醚、1,4-二恶烷、碳酸亚乙酯、碳酸亚丙酯、碳酸亚丁酯、二元酯、二乙醚、乙腈、乙酸乙酯、二甲氧基乙烷、丙酮和甲基乙基酮。在其它实施例中，溶剂包含四氢呋喃、四氢吡喃、2,5-二甲基四氢呋喃、环丁砜、N-甲基吡咯烷酮、1,3二甲基-2-咪唑啉酮、二乙二醇二甲醚、三乙二醇二甲醚、四乙二醇二甲醚、二乙二醇二丁醚、异山梨醇醚、甲基叔丁基醚、二乙醚、二苯醚、1,4-二恶烷、碳酸亚乙酯、碳酸亚丙酯、碳酸亚丁酯、二元酯、二乙醚、乙腈、乙酸乙酯、乙酸丙酯、乙酸丁酯、2-丁酮、环己酮、甲苯、二氟苯、二甲氧基乙烷、丙酮和甲基乙基酮。在某些变化形式中，溶剂为极性供给溶剂。在一种变化形式中，溶剂为THF。

[0324] 在一些实施例中，催化剂和/或溶剂流再循环到进料流或再循环到羰基化反应系统。在一些实施例中，从反应产物流再循环到羰基化反应器或进料流的溶剂和/或催化剂的部分在约0％到约100％的范围内。在一些实施例中，从反应产物流再循环到羰基化反应器或进料流的溶剂和/或催化剂的部分为约100％、约90％、约80％、约70％、约60％、约50％、约40％、约30％、约20％、约10％、或约0％。在一些实施例中，再循环与溶剂相比不同百分比的催化剂，即，催化剂或溶剂组分的比例不需要相等。

[0325] 再次参看图14中描绘的示范性系统，在一些实施例中，溶剂进料1424可将溶剂供应到羰基化反应系统入口1409。溶剂可使用泵来供应到羰基化反应系统。另外，溶剂流、源、储罐等可在惰性或CO氛围下保持。在一些实施例中，将溶剂供应到羰基化反应系统的溶剂进料可包含来自新鲜溶剂源1404的溶剂1408、来自BPL纯化系统的再循环溶剂1423、和/或来自羰基化催化剂隔离系统的再循环羰基化催化剂流1412中的溶剂。在一些实施例中，来自BPL纯化系统的再循环溶剂可存储于补充溶剂储液器中。在一些实施例中，将溶剂供应到羰基化反应系统的溶剂进料可包含来自补充溶剂储液器的溶剂。在一些实施例中，溶剂可从系统吹扫。在一些实施例中，吹扫的溶剂可为来自BPL纯化系统的再循环溶剂的溶剂。在一些实施例中，来自新鲜溶剂源的溶剂还存储到补充溶剂储液器中以用新鲜溶剂稀释来自BPL纯化系统的再循环溶剂。在一些实施例中，新鲜溶剂在进入羰基化反应系统之前从新鲜溶剂源供应到补充溶剂储液器。在一些实施例中，来自新鲜溶剂源、BPL纯化系统和羰基化

催化剂隔离系统的溶剂可通过用以移除氧和水的吸附等操作来纯化，所述氧和水可抑制羰基化催化剂。在一些实施例中，进入羰基化反应系统的所有流中的氧和/或水的量小于约500ppm、小于约250ppm、小于约100ppm、小于约50ppm、小于约20ppm、小于约10ppm、小于约5ppm、小于约2ppm、或小于约1ppm。

[0326] 在一些实施例中，新鲜溶剂源可提供至少约50kg/hr溶剂、至少约100kg/hr溶剂、至少约150kg/hr溶剂、至少约188kg/hr溶剂、至少约200kg/hr溶剂、至少约250kg/hr溶剂、至少约500kg/hr溶剂、至少约1000kg/hr溶剂、至少约1500kg/hr溶剂、至少约1880kg/hr溶剂、至少约2000kg/hr溶剂、或至少约2500kg/hr溶剂。在一些实施例中，新鲜溶剂源可提供约50kg/hr到约250kg/hr溶剂、约100kg/hr到约250kg/hr溶剂、约150kg/hr到约250kg/hr溶剂、约188kg/hr到约250kg/hr溶剂、约200kg/hr到约250kg/hr溶剂、约50kg/hr到约2500kg/hr溶剂、约100kg/hr到约2500kg/hr溶剂、约150kg/hr到约2500kg/hr溶剂、约188kg/hr到约2500kg/hr溶剂、约200kg/hr到约2500kg/hr溶剂、约250kg/hr到约2500kg/hr溶剂、约500kg/hr到约2500kg/hr溶剂、约1000kg/hr到约2500kg/hr溶剂、约1500kg/hr到约2500kg/hr溶剂、约1880kg/hr到约2500kg/hr溶剂、约2000kg/hr到约2500kg/hr溶剂、或约2250kg/hr到约2500kg/hr溶剂。在一些实施例中，新鲜溶剂源可提供约50kg/hr溶剂、约100kg/hr溶剂、约150kg/hr溶剂、约188kg/hr溶剂、约200kg/hr溶剂、约250kg/hr溶剂、约500kg/hr溶剂、约1000kg/hr溶剂、约1500kg/hr溶剂、约1880kg/hr溶剂、约2000kg/hr溶剂、或约2500kg/hr溶剂。在一些实施例中，新鲜溶剂源可提供至少约1kmol/hr溶剂、至少约2kmol/hr溶剂、至少约2.6kmol/hr溶剂、至少约3kmol/hr溶剂、至少约50kmol/hr溶剂、至少约100kmol/hr溶剂、至少约150kmol/hr溶剂、至少约250kmol/hr溶剂、至少约400kmol/hr溶剂、或至少约500kmol/hr溶剂。

[0327] 在一些实施例中，来自BPL纯化系统的再循环溶剂可提供至少约8000kg/hr溶剂、至少约9000kg/hr溶剂、至少约10000kg/hr溶剂、至少约10444kg/hr溶剂、至少约12000kg/hr溶剂、至少约80000kg/hr溶剂、至少约90000kg/hr溶剂、至少约100000kg/hr溶剂、至少约104440kg/hr溶剂、或至少约120000kg/hr溶剂。在一些实施例中，来自BPL纯化系统的再循环溶剂可提供约8000kg/hr到约12000kg/hr之间的溶剂、约9000kg/hr到约12000kg/hr之间的溶剂、约10000kg/hr到约12000kg/hr之间的溶剂、约10444kg/hr到约12000kg/hr之间的溶剂、约8000kg/hr到约120000kg/hr溶剂、约9000kg/hr到约120000kg/hr之间的溶剂、约10000kg/hr到约120000kg/hr之间的溶剂、约10444kg/hr到约120000kg/hr之间的溶剂、约12000kg/hr到约120000kg/hr之间的溶剂、约40000kg/hr到约120000kg/hr溶剂、约60000kg/hr到约120000kg/hr溶剂、约80000kg/hr到约120000kg/hr溶剂、约90000kg/hr到约120000kg/hr之间的溶剂、约100000kg/hr到约120000kg/hr之间的溶剂、约104440kg/hr到约120000kg/hr之间的溶剂、或约120000kg/hr到约120000kg/hr之间的溶剂。在一些实施例中，来自BPL纯化系统的再循环溶剂可提供约8000kg/hr溶剂、约9000kg/hr溶剂、约10000kg/hr溶剂、约10444kg/hr溶剂、或约12000kg/hr溶剂。在一些实施例中，来自BPL纯化系统的再循环溶剂可提供至少约100kmol/hr溶剂、至少约120kmol/hr溶剂、至少约140kmol/hr溶剂、至少约145kmol/hr溶剂、至少约150kmol/hr溶剂、至少250kmol/hr溶剂、至少350kmol/hr溶剂、或至少500kmol/hr溶剂。在一些实施例中，再循环溶剂流中的溶剂的质量分数可为至少约0.85、至少约0.90、至少约0.95、或至少约0.995。在一些实施例中，再

循环溶剂流中的溶剂的摩尔分数可为至少约0.85、至少约0.90、至少约0.95、至少约0.98、至少约0.99、或至少约0.993。在一些实施例中，再循环溶剂流中的溶剂的摩尔分数可为0.85到1.0、0.90到1.0、0.95到1.0、0.98到1.0、0.99到1.0、或0.993到1.0。在一些实施例中，再循环溶剂流中的溶剂的摩尔分数可为约0.85、约0.90、约0.95、约0.98、约0.99、或约0.993。来自BPL纯化系统的再循环溶剂流也可包含：不反应的一氧化碳(呈约至多0.001kg/hr、至多约0.0025kg/hr、至多约0.005kg/hr、至多约0.01kg/hr、至多0.02kg/hr、至多约0.025kg/hr、至多约0.05kg/hr、或至多约0.01kg/hr，或在0与0.005kg/hr之间、或在0与0.05kg/hr之间)，不反应的环氧乙烷(呈约至多约10kg/hr、至多约20kg/hr、至多约30kg/hr、至多约33kg/hr、至多约50kg/hr、至多约100kg/hr、至多约200kg/hr、或至多约330kg/hr，或呈约0.001到0.005、约0.02到0.004之间、或至多约0.003、至多约0.004、或至多约0.005的质量分数)，副反应产物乙醛(呈约至多3kg/hr、至多约5kg/hr、至多约8.2kg/hr、至多约10kg/hr、至多约15kg/hr、至多30kg/hr、至多约50kg/hr、或至多约82kg/hr，或呈至多约0.001、或0与8.2kg/hr之间的质量分数)，以及bPL(呈至多约2kg/hr、至多约3kg/hr、至多约5kg/hr、至多约7kg/hr、至多约10kg/hr、至多约25kg/hr、至多约50kg/hr、或至多约70kg/hr，或呈至多约0.001、或0与7kg/hr之间、或0与70kg/hr之间的质量分数)。

[0328] 在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流可提供至少约1000kg/hr溶剂、至少约1500kg/hr溶剂、至少约1700kg/hr溶剂、至少约1840kg/hr溶剂、至少约2000kg/hr溶剂、至少约5000kg/hr溶剂、至少约10000kg/hr溶剂、至少约15000kg/hr溶剂、至少约17000kg/hr溶剂、至少约18400kg/hr溶剂、或至少约20000kg/hr溶剂。在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流可提供约1000kg/hr到约2000kg/hr溶剂、约1500kg/hr到约2000kg/hr溶剂、约1700kg/hr到约2000kg/hr溶剂、约1840kg/hr到约2000kg/hr溶剂、约1000kg/hr到约20000kg/hr溶剂、约1500kg/hr到约20000kg/hr溶剂、约1700kg/hr到约20000kg/hr溶剂、约1840kg/hr到约20000kg/hr溶剂、约2000kg/hr到约20000kg/hr溶剂、约5000kg/hr到约20000kg/hr溶剂、约7500kg/hr到约20000kg/hr溶剂、约12500kg/hr到约20000kg/hr溶剂、约15000kg/hr到约20000kg/hr溶剂、或约17500kg/hr到约20000kg/hr溶剂。在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流可提供约1000kg/hr溶剂、约1500kg/hr溶剂、约1700kg/hr溶剂、约1840kg/hr溶剂、约2000kg/hr溶剂、约2500kg/hr溶剂、约3000kg/hr溶剂、约5000kg/hr溶剂、约7000kg/hr溶剂、约10000kg/hr溶剂、约12500kg/hr溶剂、约15000kg/hr溶剂、或约20000kg/hr溶剂。在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流可提供至少约10kmol/hr溶剂、至少约15kmol/hr溶剂、至少约20kmol/hr溶剂、至少约25kmol/hr溶剂、至少约30kmol/hr溶剂、至少约50kmol/hr溶剂、至少约75kmol/hr溶剂、至少约100kmol/hr溶剂、至少约150kmol/hr溶剂、至少约175kmol/hr溶剂、至少约200kmol/hr溶剂、至少约250kmol/hr溶剂、或至少约300kmol/hr溶剂。在一些实施例中，再循环羰基化催化剂流中的溶剂的质量分数可为至少约0.60、至少约0.65、至少约070、或至少约0.74。在一些实施例中，再循环羰基化催化剂流中的溶剂的摩尔分数可为至少约0.60、至少约0.65、至少约0.70、至少约0.75、至少约0.80、或至少约0.85。在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流也可包含：不反应的一氧化碳(呈约至多0.5kg/hr、至多约1kg/hr、至多约1.2kg/hr、至多约1.5kg/hr、至多5kg/hr、至多约

10kg/hr、至多约12kg/hr、或至多约15kg/hr，或呈至多约0.001的质量分数)，不反应的环氧乙烷(呈约至多约10kg/hr、至多约20kg/hr、至多30kg/hr、至多33kg/hr、至多约100kg/hr、至多约200kg/hr、至多300kg/hr、或至多330kg/hr，或呈约0.005到0.01、约0.01到0.05之间、或至多约0.014、或至多约0.10的质量分数)，副反应产物乙醛(呈约至多1kg/hr、至多约2kg/hr、至多约3.3kg/hr、至多10kg/hr、至多约20kg/hr、或至多约33kg/hr，或呈至多约0.01的质量分数)，副反应产物丁二酸酐(呈约至多1kg/hr、至多约2kg/hr、至多约3kg/hr、至多10kg/hr、至多约20kg/hr、或至多约30kg/hr，或呈至多约0.01的质量分数)，bPL(呈约至多约250kg/hr、至多约400kg/hr、至多约500kg/hr、至多约545kg/hr、至多约1000kg/hr、至多约2500kg/hr、至多约4000kg/hr、或至多约5450kg/hr，或呈至多约0.1、至多约0.15、至多约0.2、至多约0.22、或至多约0.23的质量分数)，以及羰基化催化剂或其组分。

[0329] 羰基化催化剂组分可包含例如由催化剂的降解所产生的化合物、用于产生催化剂的化合物、金属或金属离子(其为催化剂的部分)、任何有机化合物(其为催化剂的部分)、金属羰基或金属错合物(其为催化剂的部分)。举例来说，在一些实施例中，羰基化催化剂组分是羰基钴酸盐、铝沙仑化合物(aluminum salen compound)、铝卟啉化合物、铝柳酰醋氨酚化合物、钴或钴离子、或铝或铝离子，或其任何组合。

[0330] 在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流可提供至少约25kg/hr羰基化催化剂、至少约35kg/hr羰基化催化剂、至少约45kg/hr羰基化催化剂、至少约50kg/hr羰基化催化剂、至少约53kg/hr羰基化催化剂、至少约100kg/hr羰基化催化剂、至少约250kg/hr羰基化催化剂、至少约350kg/hr羰基化催化剂、至少约450kg/hr羰基化催化剂、至少约500kg/hr羰基化催化剂、至少约530kg/hr羰基化催化剂。在一些实施例中，来自羰基化催化剂隔离系统的再循环羰基化催化剂流可提供至少约0.01kmol/hr羰基化催化剂、至少约0.025kmol/hr羰基化催化剂、至少约0.04kmol/hr羰基化催化剂、至少约0.05kmol/hr羰基化催化剂、至少约0.056kmol/hr羰基化催化剂、至少约0.1kmol/hr羰基化催化剂、至少约0.25kmol/hr羰基化催化剂、至少约0.4kmol/hr羰基化催化剂、至少约0.5kmol/hr羰基化催化剂、或至少约0.56kmol/hr羰基化催化剂。在一些实施例中，再循环羰基化催化剂流中的羰基化催化剂的质量分数可为至少约0.002、至少约0.015、至少约0.02、或至少约0.022。在一些实施例中，再循环羰基化催化剂流中的羰基化催化剂的摩尔分数可为至少约0.0002、至少约0.0015、至少约0.002、至少约0.003、至少约0.004、或至少约0.005。

[0331] 在一些实施例中，羰基化反应系统的入口可以至少约10000kg/hr、至少约11000kg/hr、至少约12000kg/hr、至少约12250kg/hr、至少约13000kg/hr、至少约25000kg/hr、至少约50000kg/hr、至少约100000kg/hr、至少约110000kg/hr、至少约120000kg/hr、至少约122500kg/hr、或至少约130000kg/hr接收来自溶剂进料1424的溶剂。在一些实施例中，羰基化反应系统的入口可以至少约150kmol/hr、至少约160kmol/hr、至少约170kmol/hr、至少约180kmol/hr、至少约190kmol/hr、至少约500kmol/hr、至少约1000kmol/hr、至少约1500kmol/hr、至少约1600kmol/hr、至少约1700kmol/hr、至少约1800kmol/hr、或至少约1900kmol/hr接收来自溶剂进料的溶剂。在一些实施例中，可固定供应到羰基化反应系统的溶剂中的溶剂的量以确保羰基化反应系统中的滞留时间为设定时间。举例来说，滞留时间可为约1到500分钟、约20到450分钟、约30到300分钟、约35到200分钟、或约40到80分钟。如

先前论述，在一些实施例中，引入到羰基化反应系统中的溶剂可包含来自羰基化催化剂隔离系统和BPL纯化系统的一些再循环溶剂。因此，在一些实施例中，羰基化反应系统的入口也可接收：一氧化碳(呈约0.1到10kg/hr、约0.5到5kg/hr、约0.1到10kg/hr、约0.1到50kg/hr、约0.1到100kg/hr、约0.5到50kg/hr、至多约50kg/hr、至多约10kg/hr、至多约5kg/hr、至多约3kg/hr、或至多约1.3kg/hr)，环氧乙烷(呈约40到80kg/hr、约50到70kg/hr、约40到150kg/hr、约40到250kg/hr、约50到500kg/hr、约50到800kg/hr、至多约800kg/hr、至多约500kg/hr、至多约250kg/hr、80kg/hr、至多约70kg/hr、或至多约66kg/hr，或呈约0.001到0.01、约0.002到0.007、或至多约0.01、至多约0.005的质量分数)，乙醛(呈约1到200kg/hr、约1到150kg/hr、约1到100kg/hr、约1到50kg/hr、约1到20kg/hr、约5到15kg/hr、或至多约200kg/hr、至多约150kg/hr、至多约100kg/hr、至多约50kg/hr、至多约20kg/hr、至多约15kg/hr、或至多约11kg/hr，或呈至多约0.001的质量分数)，丁二酸酐(呈约1到100kg/hr、约1到50kg/hr、1到10kg/hr、约1到5kg/hr、或至多约50kg/hr、至多约10kg/hr、5kg/hr、或至多约3kg/hr)，bPL(呈约至多2000kg/hr、至多约1500kg/hr、至多约1000kg/hr、至多约500kg/hr、200kg/hr、至多约300kg/hr、至多约500kg/hr、至多约550kg/hr、或至多约600kg/hr，或呈至多0.1、至多约0.075、至多约0.05、或至多约0.043的质量分数)，以及来自溶剂进料的羰基化催化剂或其组分。在一些实施例中，来自溶剂进料的溶剂的质量分数可为至少约0.85、至少约0.9、至少约0.94、或至少约0.95。在一些实施例中，来自溶剂进料的溶剂的摩尔分数可为至少约0.85、至少约0.9、至少约0.94、或至少约0.95。

[0332] 在一些实施例中，羰基化反应系统的入口可以至少约1000kg/hr、至少约750kg/hr、至少约600kg/hr、至少约530kg/hr、至少约500kg/hr、至少约250kg/hr、至少约100kg/hr、至少约75kg/hr、至少约60kg/hr、至少约53kg/hr、或至少约50kg/hr接收来自溶剂进料的羰基化催化剂。在一些实施例中，羰基化反应系统的入口可以至少约1kmol/hr、至少约0.8kmol/hr、至少约0.75kmol/hr、至少约0.56kmol/hr、或至少约0.5kmol/hr、至少约0.25kmol/hr、至少约0.1kmol/hr、至少约0.1kmol/hr、至少约0.075kmol/hr、至少约0.056kmol/hr、或至少约0.05kmol/hr接收来自溶剂进料的羰基化催化剂。在一些实施例中，来自溶剂进料的羰基化催化剂的质量分数可为至少约0.0002、至少约0.002、至少约0.003、或至少约0.004。

[0333] 在一些实施例中，羰基化反应系统的入口可在约10到100℃之间、约20到50℃之间、约25到45℃之间、约30到40℃之间、或约36.6℃的温度下接收溶剂进料。在一些实施例中，羰基化反应系统的入口可在至少约50巴、约60到70巴、或至少约65巴的压力下接收溶剂进料。

[0334] 其它进料源

[0335] β-丙内酯生产系统/生产方法可进一步包含其它进料源。举例来说，在一种变化形式中，β-丙内酯生产系统/生产方法进一步包含路易斯碱添加剂源。

[0336] 在一些实施例中，路易斯碱添加剂可添加到羰基化反应器。在某些实施例中，这类路易斯碱添加剂可使催化剂稳定或减少催化剂的失活。在一些实施例中，路易斯碱添加剂选自由以下组成的群组：膦、胺、胍、脒和含氮杂环。在一些实施例中，路易斯碱添加剂为受阻胺碱。在一些实施例中，路易斯碱添加剂为2,6-二甲基吡啶、咪唑、1-甲基咪唑、4-二甲胺基吡啶、三己胺和三苯膦。

[0337] 图14中描绘的示范性系统还包含羰基化产物流1414、隔离后的羰基化产物流1416、BPL纯化流1418、PPL产物流1420和GAA产物流1422。

[0338] 反应器

[0339] 在一些实施例中，羰基化反应系统可包含用于羰基化反应的至少一个反应器。在一些实施例中，羰基化系统可包含用于羰基化反应的串联和/或并联的多个反应器。在一些实施例中，一或多个反应器可为一或多个连续的反应器。合适的连续反应器的实例包含但不限于管式反应器(即，推流型反应器)、固定床反应器、流化床反应器、连续搅拌罐反应器(“CSTR”)、热交换器反应器(例如，壳管型反应器)、环流反应器(例如，总线(Buss)、喷射等)、膜反应器或所属领域的技术人员已知的其它反应器。在一些实施例中，羰基化反应系统包含一或多个CSTR。羰基化反应系统的所有入口和出口可包含传感器，所述传感器可确定流动速率、组合物(尤其水和/或氧含量)、温度、压力和所属领域的技术人员已知的其它变量。另外，传感器可连接到控制单元，所述控制单元可控制各种流(即，进料控制)，以便基于由传感器单元所确定的过程的需要来调整过程。这类控制单元可调整质量以及系统的过程控制。

[0340] 在一些变化形式中，β-丙内酯生产系统/生产方法中的反应器被配置成以某些比率接收催化剂、环氧乙烷和一氧化碳。在一些实施例中，基于其它反应条件选择催化剂比环氧乙烷的比率，以使得反应以低成本和时间可行的方式进行。在一些实施例中，催化剂比环氧乙烷的比率以摩尔计为约1:10000在一些实施例中，催化剂比环氧乙烷的摩尔比为约1:5000、约1:2500、约1:2000、约1:1500、约1:1000、约1:750、约1:500、约1:250、约1:200、约1:150、或约1:100。在一些实施例中，环氧乙烷的浓度在约0.1M与约5.0M之间的范围内。在一些实施例中，环氧乙烷的浓度在约0.5M与约3.0M之间的范围内。

[0341] 在某些实施例中，反应流中的一氧化碳比环氧乙烷的摩尔比在约0.1:1到约100:1的范围内。在某些实施例中，反应流中的一氧化碳比环氧乙烷的摩尔比为约50:1、约20:1、约10:1、约5:1、或约1:1，或在包含这些比率中的任何两个的范围内。在一些实施例中，基于其它反应条件选择一氧化碳比环氧乙烷的比率，以使得反应以低成本和时间可行的方式进行。

[0342] 在一些变化形式中，β-丙内酯生产系统/生产方法中的反应器被配置成进一步接收一或多种额外组分。在某些实施例中，额外组分包含不直接地参与环氧乙烷的化学反应的稀释剂。在某些实施例中，这类稀释剂可包含一或多种惰性气体(例如，氮、氩、氦等等)或易失性有机分子，所述易失性有机分子如烃、醚等等。在某些实施例中，反应流可包括氢、二氧化碳的一氧化碳、甲烷、以及通常在工业一氧化碳流中找到的其它化合物。在某些实施例中，这类额外组分可在将环氧乙烷转化成β-丙内酯和各种终端产物所涉及的过程中的一个或多个中具有直接或间接化学作用。额外反应物也可包含一氧化碳与另一气体的混合物。举例来说，如上文所提及，在某些实施例中，一氧化碳以与氢的混合物(例如，合成气)提供。

[0343] 因为羰基化反应发热，所以所使用的反应器可包含用于反应物料冷却的外部循环环流。在一些实施例中，反应器也可包含用于冷却的内部热交换器。举例来说，就壳管型反应器而言，反应器可流过反应器的管部分，且冷却介质可流过反应器的壳层或反之亦然。热交换器系统可取决于布局、反应器选择以及反应器的物理位置而变化。反应器可在反应器外部采用热交换器，以便执行冷却/加热，或反应器可具有集成的热交换器，如管和壳层反

应器。举例来说,CSTR可利用用于通过将反应流体的一部分泵送过外部热交换器来散热的布局,或推流型反应器可为将反应器和热交换器组合成单一单元的集成的单元。额外反应器/热交换器系统和热管理系统可在US专利第3,128,163号、第4,759,313号、第8,246,915号中找到,其以全文引用的方式并入本文中。在一些实施例中,热可通过使用以下来从CSTR中移除:反应器夹套、一或多个内部冷却盘管、较低温度进料和/或再循环流中的冷却剂,在泵包围环流情况下的外部热交换,和/或由所属领域的技术人员已知的其它方法。在一些实施例中,热可通过使用反应器夹套和/或内部冷却盘管中的冷却剂来从推流型反应器或环流反应中移除。此外,反应可出现在壳管式反应器的管侧或壳侧,且另一侧可具有冷却介质。另外,反应器可具有多个冷却区和流,所述冷却区具有变化的热传递区域和/或热传递流体温度。

[0344] 所采用的反应器的类型和所采用的热交换器的类型(外部或集成的)可随各种化学考虑因素(例如,反应转化率、副产物等)、所产生的放热程度和反应的混合需求而变。

[0345] 因为羰基化反应为发热的反应,且BPL纯化系统和热分解需要能量,所以有可能在羰基化反应系统与BPL纯化系统和/或热分解系统之间集成组分中的至少一些。举例来说,蒸汽或调温水或其它适当热传递介质可产生于羰基化反应系统的热交换器中且传输到BPL纯化系统供用于加热例如蒸馏柱。另外,BPL纯化系统和羰基化反应系统可集成到单一系统或单元中,以使得由羰基化反应产生的热可用于BPL纯化系统(用于蒸发器或蒸馏柱)。蒸汽可经过反应液体与热交换器的水/蒸汽之间的温度梯度而产生于热交换器(例如,壳管式热交换器、反应器的冷却夹套等)中。蒸汽可用于发热的单元(羰基化反应、聚合反应)与吸热单元(BPL纯化系统的柱/蒸发器和热分解反应)之间的热集成。在一些实施例中,蒸汽仅用于热管理和集成,且将不直接地引入到生产方法中。

[0346] 如先前描述,水和氧可破坏羰基化催化剂。因而,还应最小化氧和水浸入到羰基化系统中。因而,反应器密封可利用磁力驱动、双机械密封和/或与羰基化反应的反应物和产物相容但不可渗透到大气的建构材料。在一些实施例中,反应器的建构材料包含金属。在一些实施例中,金属可为不锈钢。在一些实施例中,金属可为碳钢。在一些实施例中,金属可为金属合金,如镍合金。在一些实施例中,当相容性或方法条件指示例如高氯化物含量时或如果碳钢催化EO分解,那么选择金属。在一些实施例中,一切直到聚合反应系统可包含碳钢。碳钢超过不锈钢的益处中的一个为其成本。在一些实施例中,金属可具有表面涂层以便最小化聚合物成核位置。反应器的建构材料也可包含弹性体密封。在一些实施例中,弹性体密封与羰基化反应的反应物和产物相容但不可渗透到大气。弹性体密封的实例包含但不限于卡乐瑞(Kalrez)6375、科拉兹(Chemraz)505、PTFE囊封的氟化橡胶(Viton)和PEEK。羰基化反应系统的外部部分的建构材料可与环境相容,例如与沙、盐水相容,不吸热,且可保护设备免受环境影响。

[0347] 在一些实施例中,操作羰基化反应系统,以便在聚合反应系统之前最小化或减缓PPL和聚氧化乙烯形成。在一些实施例中,操作羰基化反应系统,以便避免催化剂分解。

[0348] 在一些实施例中,一或多个羰基化反应器可具有下游闪蒸罐以将不反应的一氧化碳从羰基化反应系统分离为再循环一氧化碳流,所述下游闪蒸罐具有回流冷凝器。如先前描述,再循环一氧化碳流可传送到CO压缩机且/或在传送回羰基化反应系统中之前与新鲜一氧化碳进料组合。闪蒸罐可将大部分CO分离以避免其在下游分离,尤其在羰基化催化剂

隔离系统中。在一些实施例中，过量气体从反应器自身移除或吹扫，且由此闪蒸罐不是必需的。

[0349] 在一些实施例中，一或多个羰基化反应器可在约40到100℃、约50到90℃、约60到80℃、约65到75℃、或约70℃的温度下操作。在一些实施例中，反应温度可在约-20℃到约600℃之间的范围内。在一些实施例中，反应温度为约-20℃、约0℃、约20℃、约40℃、约60℃、约80℃、约100℃、约200℃、约300℃、约400℃、约500℃、或约600℃。在一些实施例中，温度在约40℃与约120℃之间的范围内。在一些实施例中，温度在约60℃与约140℃之间的范围内。在一些实施例中，温度在约40℃与约80℃之间的范围内。在一些实施例中，温度在约50℃与约70℃之间的范围内。在一些实施例中，反应物、催化剂和溶剂在标准温度下供应到反应器，且随后在反应器中加热。在一些实施例中，反应物在进入反应器之前预热。

[0350] 在一些实施例中，一或多个羰基化反应器可在约600到1200psig、约700到1100psig、约800到1000psig、约850到950psig、或约900psig的压力下操作。在一些实施例中，反应压力可在约50psig到约5000psig之间的范围内。在一些实施例中，反应压力为约100psig、约200psig、约300psig、约400psig、约500psig、约600psig、约700psig、约800psig、约900psig、或约1000psig。在一些实施例中，压力在约50psig到约2000psig的范围内。在一些实施例中，压力在约100psig到1000psig的范围内。在一些实施例中，压力在约200psig到约800psig的范围内。在一些实施例中，压力在约800psig到约1600psig的范围内。在一些实施例中，压力在约1500psig到约3500psig的范围内。在一些实施例中，压力在约3000psig到约5500psig的范围内。在一些实施例中，反应压力全部由一氧化碳供应。举例来说，一氧化碳在高压力下添加到反应器以将压力增加到反应压力。在一些实施例中，所有反应物、溶剂和催化剂在反应压力下供应到反应器。

[0351] 在一些实施例中，反应基于反应动力学和/或反应条件保持一段时间，足以使环氧乙烷完全反应、近乎完全反应成羰基化产物或尽可能完全反应。在一些实施例中，反应时间为步骤(a)中的羰基化反应器中的滞留时间。在某些实施例中，滞留时间为约12小时、约8小时、约6小时、约3小时、约2小时、或约1小时。在某些实施例中，滞留时间为约30分钟、约20分钟、约15分钟、约10分钟、约5分钟、约3分钟、约2分钟、或约1分钟。在某些实施例中，滞留时间小于1分钟。

[0352] 羰基化反应系统所涉及的化学可包含但不限于以下三个反应：(1)CO+EO→bPL；(2)EO→乙醛；(3)bPL→丁二酸酐。三个反应的转化率可取决于包含以下的多种因素而变化：反应物的量、催化剂的量、温度、压力、流动速率等。然而，第一个反应可具有约0.2到0.999、约0.5到0.95、约0.6到0.9、约0.7到0.8、或约0.75的EO转化率。第二个反应可具有约0到0.1、约0.001到0.02、约0.002到0.01、或约0.005的EO转化率。第三个反应可具有约0.0002到0.02、约0.0005到0.01、约0.001到0.003、或约0.002的bPL转化率。

[0353] 图15绘示本文中所公开的羰基化反应系统的示范性实施例。羰基化反应系统1513可包含用于羰基化反应器1525的羰基化反应系统入口1509。如先前描述，入口可由多个入口组成或供应到反应系统中。另外，羰基化反应系统1513包含闪蒸罐1526以及冷凝器1527。闪蒸罐1526和冷凝器1527将反应器产物流分离到再循环一氧化碳流1510和羰基化产物流1514中。

[0354] 羰基化产物流(即，BPL产物流)

[0355] 在一些实施例中，羰基化产物流包含至少约2000kg/hr bPL、至少约2500kg/hr bPL、至少约3000kg/hr bPL、至少约3500kg/hr bPL、至少约3638kg/hr bPL、至少约4000kg/hr bPL、至少约8000kg/hr bPL、至少约12000kg/hr bPL、至少约16000kg/hr bPL、至少约20000kg/hr bPL、至少约25000kg/hr bPL、至少约30000kg/hr bPL、至少约35000kg/hr bPL、至少约36380kg/hr bPL、或至少约40000kg/hr bPL。在一些实施例中，羰基化产物流包含在约2000kg/hr bPL与约4000kg/hr bPL、约2500kg/hr bPL与约4000kg/hr bPL、约3000kg/hr bPL与约4000kg/hr bPL、约3500kg/hr bPL与约4000kg/hr bPL、约3638kg/hr bPL与约4000kg/hr bPL之间、在约2000kg/hr bPL与约40000kg/hr bPL、约2500kg/hr bPL与约40000kg/hr bPL、约3000kg/hr bPL与约40000kg/hr bPL、约3500kg/hr bPL与约40000kg/hr bPL、约3638kg/hr bPL与约40000kg/hr bPL、约4000kg/hr bPL与约40000kg/hr bPL、约8000kg/hr bPL与约40000kg/hr bPL、约12000kg/hr bPL与约40000kg/hr bPL、约16000kg/hr bPL与约40000kg/hr bPL、约20000kg/hr bPL与约40000kg/hr bPL、约25000kg/hr bPL与约40000kg/hr bPL、约30000kg/hr bPL与约40000kg/hr bPL、或约35000kg/hr bPL与约40000kg/hr bPL之间。

[0356] 在一些实施例中，羰基化产物流包含至少约30kmol/hr bPL、至少约40kmol/hr bPL、至少约45kmol/hr bPL、至少约50kmol/hr bPL、至少约55kmol/hr bPL、至少约100kmol/hr bPL、至少约200kmol/hr bPL、至少约300kmol/hr bPL、至少约400kmol/hr bPL、至少约450kmol/hr bPL、至少约500kmol/hr bPL、或至少约550kmol/hr bPL。在一些实施例中，羰基化产物流中的bPL的质量分数可为约0.1到0.4、约0.15到0.3、约0.18到0.25、约0.2到0.23、至少约0.15、至少约0.2、或至少约0.224。在一些实施例中，羰基化产物流中的bPL的摩尔分数可为约0.1到0.4、约0.15到0.3、约0.18到0.25、约0.21到0.23、至少约0.15、至少约0.2、或至少约0.22。羰基化产物流也可包含其它组分，所述其它组分包含：不反应的环氧乙烷(呈约0.005到0.05、约0.02到0.045、约0.04、至多约0.014、至多约0.02、或至多约0.05的质量分数)，不反应的一氧化碳(呈约0.0005到0.01、至多约0.01、或至多约0.02的质量分数)，乙醛(呈约0.0005到0.001、至多约0.001、或至多约0.002的质量分数)，丁二酸酐(呈约0.0005到0.001、至多约0.001、或至多约0.002的质量分数)，羰基化催化剂(呈约40到640kg/hr、约45到600kg/hr、约50到600kg/hr、约50到300kg/hr、约50到100kg/hr、约40到64kg/hr、约45到60kg/hr、约50到60kg/hr、至多54.8kg/hr、至多约60kg/hr、至多300kg/hr、或至多600kg/hr，或呈约0.001到0.005、约0.002到0.004、至多约0.003、或至多约0.004的质量分数)，以及剩余溶剂。在一些实施例中，羰基化产物流可包含足够的环氧乙烷以便预防形成酐。

[0357] 在一些实施例中，来自羰基化反应系统的羰基化产物流可具有约50到100℃、约60到90℃、约65到75℃、或约70℃的温度。在一些实施例中，羰基化产物流可具有约1到5巴、约2到4巴、或约3巴的压力。

[0358] 在一些实施例中，羰基化反应系统具有至少约95％、至少约97％、至少约99％、至少约99.5％、或至少约99.8％的选择性。在一些实施例中，羰基化反应系统具有至少约90％、至少约95％、至少约98％、至少约99％、或至少约99.5％的产率。在一些实施例中，bPL的选择性为bPL产率比环氧乙烷转化率的比率，其中bPL产率相对于环氧乙烷来测量。在其它实施例中，bPL的选择性为bPL产率比一氧化碳转化率的比率，其中bPL产率相对于一氧化

碳来测量。

[0359] 羰基化催化剂再循环系统

[0360] 再次参考图1,羰基化催化剂再循环系统可用于回收存在于β-丙内酯产物流中的羰基化催化剂或其组分的至少一部分。这类回收羰基化催化剂可在β-丙内酯生产系统/生产方法中再循环和再使用。

[0361] 羰基化催化剂组分可包含例如由催化剂的降解所产生的化合物、用于产生催化剂的化合物、金属或金属离子(其为催化剂的部分)、任何有机化合物(其为催化剂的部分)、金属羰基或金属错合物(其为催化剂的部分)。举例来说,在一些实施例中,羰基化催化剂组分是羰基钴酸盐、铝沙仑化合物、铝卟啉化合物、铝柳酰醋氨酚化合物、钴或钴离子、或铝或铝离子,或其任何组合。

[0362] 所属领域中已知的任何合适的方法和技术可用于回收存在于β-丙内酯产物流中的羰基化催化剂的至少一部分。这类方法和技术可包含例如纳米过滤(如图1中所描绘)、蒸馏、液-液萃取、离子液体和离子交换、或吸附。也可采用本文中所描述的方法和技术的组合。

[0363] 纳米过滤

[0364] 在一些实施例中,羰基化催化剂再循环系统涉及使用纳米过滤。举例来说,可使用纳米过滤膜。在一些变化形式中,纳米过滤膜为有机溶剂稳定的纳米过滤膜。尽管任何纳米过滤膜可与和羰基化反应相容的任何有机溶剂或有机溶剂系统组合使用,但纳米过滤膜可与有机溶剂或溶剂组合来选择,以使得方法实现预定水平的内酯形成和催化剂-内酯分离。在一些变化形式中,纳米过滤膜为聚合纳米过滤膜,而在其它变化形式中,纳米过滤膜为陶瓷纳米过滤膜。

[0365] 在一些实施例中,纳米过滤膜为聚合膜。任何合适的聚合膜可用于本文中所描述的方法。举例来说,在一些变化形式中,聚合膜包括聚酰亚胺、聚酰胺-酰亚胺、硅酮涂布的聚酰胺复合物、聚丙烯腈、聚丙烯腈载体上的聚二甲基硅氧烷薄膜、硅酮、聚磷腈、聚苯硫醚、聚醚醚酮、或聚苯并咪唑(polybenzimidazol)。在某些变化形式中,聚合膜具有聚硅氧主链。

[0366] 在某些变化形式中,聚合膜选自聚酰亚胺,包含由膜萃取技术有限公司(Membrane Extraction Technology Ltd)(英国温布利(Wembley,UK))出售的商标为STARMEM的那些聚合膜和由以下制成的一体地去皮不对称膜:聚酰亚胺、聚酰胺-酰亚胺、硅酮涂布的聚酰胺复合物、聚丙烯腈、聚丙烯腈载体上的聚二甲基硅氧烷薄膜、硅酮、聚磷腈、聚苯硫醚、聚醚醚酮和聚苯并咪唑。在一些实施例中,有机溶剂为四氢呋喃,且纳米过滤膜为由兰精(Lenzing)P84或ST ARMEM®聚酰亚胺膜制成的一体地去皮不对称聚酰亚胺膜。在一些实施例中,有机溶剂乙醚,且纳米膜为硅酮涂布的聚酰胺复合物。在一些实施例中,纳米过滤膜为可商购的膜。在其它实施例中,纳米过滤膜为由兰精(Lenzing)P84制成且由GMT膜科技股份有限公司(GMT Membrantechnik GmbH)(德国莱茵费尔登(Rheinfelden,Germany))制造的一体地去皮不对称聚酰亚胺膜。在一些其它实施例中,纳米过滤膜为来自膜萃取技术有限公司(Membrane Extraction Technology Ltd)(温布利(Wembley),英国(UK))的STARMEM®聚酰亚胺膜,且纳米过滤步骤在低于50℃的温度和低于60巴的压力下进行。在其它实施例中,纳米过滤膜为如美国专利第6,887,380号中所公开的硅酮涂布的有机溶

剂抗性聚酰胺复合物纳米过滤膜，所述专利以引入的方式并入本文中。

[0367] 在其它变化形式中，纳米过滤膜为包括无机材料的陶瓷膜。

[0368] 各种配置的纳米过滤膜可用于羰基化催化剂再循环系统中。举例来说，在一些实施例中，膜为板和框式膜。参考图3，描述使用膜310的示范性羰基化催化剂再循环系统300。进料302可包含例如β-丙内酯、羰基化溶剂、少量环氧乙烷和一氧化碳、羰基化催化剂以及副产物(如乙醛和丁二酸酐)。进料302通过泵306和308来转移到膜。传感器304放置在泵306之前以调控进料302泵送过膜310的速率。在一些变化形式中，传感器304可为紫外(UV)传感器。也可采用其它合适的传感器。进料302借助于根据泵设定点变化的跨膜压来穿过膜310。在一些变化形式中，膜310为板和框式膜，如图3中所描绘。然而，在其它变化形式中，可使用其它合适的膜。举例来说，在其它变化形式中，羰基化催化剂再循环系统300的膜310可为螺旋卷绕式膜或管状膜，且这类替代的配置在下文进一步详细论述。

[0369] 再次参考图3，膜310产生渗透液流316和保留物流324。渗透液流316可包含例如β-丙内酯、羰基化溶剂、少量环氧乙烷和一氧化碳、副产物(如乙醛和丁二酸酐)以及痕量羰基化催化剂。另外，渗透液流316可具有至少0.5L/m^2hr巴、至少0.6L/m^2hr巴、至少0.7L/m^2hr巴、至少0.8L/m^2hr巴、至少0.9L/m^2hr巴、至少1.0L/m^2hr巴、至少1.1L/m^2hr巴、至少1.2L/m^2hr巴、至少1.3L/m^2hr巴、至少1.4L/m^2hr巴、至少1.5L/m^2hr巴、至少1.6L/m^2hr巴、至少1.7L/m^2hr巴、至少1.8L/m^2hr巴、至少1.9L/m^2hr巴、至少2L/m^2hr巴、至少2.5L/m^2hr巴、至少3L/m^2hr巴、至少3.5L/m^2hr巴、或至少4L/m^2hr巴、或0.5L/m^2hr巴与5L/m^2hr巴之间、或3L/m^2hr巴与4.5L/m^2hr巴之间、或0.5L/m^2hr巴与10L/m^2hr巴之间、或3L/m^2hr巴与10L/m^2hr巴之间的渗透率。在一些变化形式中，渗透率(或膜渗透率)是指在指定跨膜压(TMP)下渗透过指定表面积的材料的体积流率。在一些变化形式中，跨膜压为膜的保留物面与膜的渗透物面之间的压力差。在一些实施例中，关系可表达为渗透率＝体积流率/(表面积×TMP)。在一些实施例中，渗透率可通过测量在已知TMP下渗透过已知表面积的膜样本的材料的流动速率来确定。

[0370] 传感器312放置在膜310之后以分析渗透液流316的含量。在一些变化形式中，传感器312可为UV传感器。也可采用其它合适的传感器。

[0371] 羰基化催化剂再循环系统300被配置成实现至少80％、至少85％、至少90％、至少91％、至少92％、至少93％、至少94％、至少95％、至少96％、至少97％、至少98％、至少99％、至少99.1％、至少99.2％、至少99.3％、至少99.4％、至少99.5％、至少99.6％、至少99.7％、至少99.8％、或至少99.9％、或100％催化剂排出。在一些变化形式中，催化剂排出是指渗透过膜的催化剂与不渗透过膜且保持在膜的保留物面上的催化剂相比的百分比(按质量计)。催化剂排出可通过所属领域中的任何合适的方法来确定，所述方法包含例如使用分析工具来检测膜进料、渗透物和保留物处的催化剂浓度。

[0372] 再次参考图3，压力控制阀314放置在传感器312之后且偏置到上游闪蒸单元。在一些实施例中，压力控制阀(PCV)314可用于控制可影响膜的性能跨膜压(TMP)。传感器312可检测催化剂排出且将反馈信号提供到PCV 314，以对系统性能进行调整。PCV 314可在一些实施例中检测上游闪蒸罐的压力且预防易失性物种(例如，一氧化碳)随着压力在膜中改变而汽化。膜中的汽化或闪蒸可影响膜的耐久性。

[0373] 保留物流324可包含例如羰基化溶剂、β-丙内酯和羰基化催化剂。泵322可用于将

保留物流324转移到本文中所描述的β-丙内酯生产系统/生产方法(例如,β-丙内酯生产系统/生产方法的转移到羰基化反应器)。在一些实施例中,催化剂可随着循环过保留物面上的膜系统(例如,在暴露于氧或水的情况下)而钝化。在某些实施例中,保留物流的一部分吹扫一段时间以避免在系统内积聚失活的催化剂。阀320被配置成吹扫系统和渗出326。

[0374] 如上文所论述,图3描绘使用板和框式膜,但可采用其它膜配置。举例来说,在其它实施例中,膜为螺旋卷绕式膜。在其它实施例中,膜为管状膜。在其它实施例中,膜为褶状薄片膜。

[0375] 在一种变化形式中,膜为呈板和框式配置的聚合膜。在另一变化形式中,膜为呈螺旋卷绕式配置的聚合膜。在又另一变化形式中,膜为呈管状配置的陶瓷膜。

[0376] 尽管图3描绘使用一张膜,但在其它变化形式中,可使用多张膜。举例来说,可使用串联连接的至少两张膜。在一种变化形式中,可使用串联连接的多张板和框式膜。在其它变化形式中,可使用串联连接的多张螺旋卷绕式膜。在其它变化形式中,板和框式膜可与螺旋卷绕式膜串联连接。应理解,膜配置可为串联、并联或呈串联与并联的组合。举例来说,在一些实施例中,膜配置于“圣诞树”配置中。

[0377] 在一个实施例中,纳米过滤膜为具有硅酮主链、至少99%的羰基化催化剂排出率和至少1L/m^2hr巴的渗透率的聚合螺旋卷绕式膜。

[0378] 蒸馏

[0379] 在其它实施例中,羰基化催化剂再循环系统涉及蒸馏设备。

[0380] 在一些变化形式中,蒸馏设备使用多溶剂系统来回收存在于β-丙内酯产物流中的羰基化催化剂的至少一部分。举例来说,在一种变化形式中,可使用两种溶剂系统,其中第一溶剂具有高于166℃的沸点且可充当催化剂的载剂,且选择第二溶剂以促进羰基化反应。

[0381] 在其它变化形式中,蒸馏可包含加热β-丙内酯产物流以使β-丙内酯的至少一部分和/或溶剂挥发,以形成馏出物,移除馏出物,且使馏出物冷凝。在其它实施例中,蒸馏为真空蒸馏,其中馏出物通过减少β-丙内酯产物流的压力而形成。在某些实施例中,真空蒸馏允许羰基化催化剂的至少一部分在较高温度下从β-丙内酯产物流中移除而不降解催化剂。在其它变化形式中,蒸馏通过既增加温度又减小β-丙内酯产物流的压力来进行。在蒸馏之后剩余在滞留的混合物中的羰基化催化剂可随后使用所属领域中已知的任何方法来分离供再用于羰基化反应,所述方法包含例如溶剂-溶剂萃取、纳米过滤、离子液体、或吸附。

[0382] 液-液萃取

[0383] 在其它实施例中,羰基化催化剂再循环系统涉及液-液萃取设备。

[0384] 在一些变化形式中,液-液萃取设备采用萃取溶剂,催化剂(催化剂的组分)可溶或至少部分可溶于所述萃取溶剂。在其它变化形式中,萃取溶剂为β-丙内酯可溶或至少部分可溶于其中的一种萃取溶剂,但所述萃取溶剂具有极少溶解羰基化催化剂(或羰基化催化剂的一或多种组分)的倾向。在任一情况下,使用萃取溶剂使得形成两个阶段。在某些实施例中,萃取溶剂为如水或离子液体的高度极性溶剂。在某些实施例中,萃取溶剂为超临界CO_2。在某些实施例中,萃取溶剂为水或水溶液。在某些实施例中,萃取溶剂为离子液体。在某些实施例中,当溶剂为离子液体时,离子液体具有式$[Cat^+][X^-]$,其中$[Cat^+]$是指一或多种有机阳离子物种;以及$[X^-]$是指一或多种阴离子。在某些实施例中,$[Cat^+]$选自由以下组成的群组:铵、四烷基铵、苯并咪唑鎓、苯并呋喃鎓(benzofuranium)、苯并噻吩鎓

(benzothiophenium)、苯并三唑鎓(benzotriazolium)、硼杂环戊二烯鎓(borolium)、噌啉鎓(cinnolinium)、二氮杂二环癸烯鎓(diazabicyclodecenium)、二氮杂二环壬烯鎓(diazabicyclononenium)、1,4-二氮杂二环[2.2.2]辛烷鎓(1,4-diazabicyclo[2.2.2]octanium)、二氮杂二环-十一烯鎓(diazabicyclo-undecenium)、二噻唑鎓(dithiazolium)、呋喃鎓(furanium)、胍鎓(guanidinium)、咪唑鎓(imidazolium)、吲唑鎓(indazolium)、吲哚啉鎓(indolinium)、吲哚鎓(indolium)、吗啉鎓(morpholinium)、氧杂硼杂环戊二烯鎓(oxaborolium)、氧杂磷脂鎓(oxaphospholium)、噁嗪鎓(oxazinium)、噁唑鎓(oxazolium)、异-噁唑鎓(iso-oxazolium)、氧代噻唑鎓(oxothiazolium)、磷脂鎓(phospholium)、鏻鎓(phosphonium)、酞嗪鎓(phthalazinium)、哌嗪鎓(piperazinium)、哌啶鎓、吡喃鎓(pyranium)、吡嗪鎓(pyrazinium)、吡唑鎓、哒嗪鎓(pyridazinium)、吡啶鎓(pyridinium)、嘧啶鎓(pyrimidinium)、吡咯烷鎓(pyrrolidinium)、吡咯鎓(pyrrolium)、喹唑啉鎓(quinazolinium)、喹啉鎓(quinolinium)、异-喹啉鎓(iso-quinolinium)、喹喔啉鎓(quinoxalinium)、喹宁环鎓(quinuclidinium)、硒唑鎓(selenazolium)、硫鎓(sulfonium)、四唑鎓(tetrazolium)、噻二唑鎓(thiadiazolium)、异-噻二唑鎓(iso-thiadiazolium)、噻嗪鎓(thiazinium)、噻唑鎓(thiazolium)、异噻唑鎓(iso-thiazolium)、噻吩鎓(thiophenium)、硫脲鎓(thiuronium)、三嗪鎓(triazinium)、三唑鎓(triazolium)、异三唑鎓(iso-triazolium)、脲鎓(uronium)以及这些中的两种或更多种的任何组合。根据本发明,[X″]可包括选自以下的阴离子:卤化物、硫酸根、磺酸根、磺酰亚胺、磷酸根、膦酸根、羧酸根、CN^-、NO_3^-、NO_2^-、BF_4^-和PF_6^-。

[0385] 在一些实施例中,萃取溶剂包含戊烷、环己烷、己烷、庚烷、四氢呋喃、对-二噁烷、4-甲基-1,3-二氧环戊-2-酮、N,N-二甲基甲酰胺、1-甲基-2-吡咯烷酮、或环丁砜,或其任何组合。在一个实施例中,萃取溶剂包含环丁砜和己烷。在另一实施例中,液-液萃取溶剂包含环丁砜、己烷和二噁烷。

[0386] 沉淀

[0387] 在某些实施例中,羰基化催化剂再循环系统被配置成使羰基化催化剂沉淀。羰基化催化剂的沉淀可通过已知方法和技术来实现。沉淀催化剂的合适的手段对熟练的化学工作者而言将显而易见,且可包含但不限于:将溶剂添加到催化剂催化剂或其组分)难溶于其中的β-丙内酯产物流,冷却β-丙内酯产物流,添加与催化剂(或其组分)相互作用的材料以形成不溶的加合物,将溶剂、过量原料、或一氧化碳从β-丙内酯产物流中移除,以及这些手段中的任何两个或大于两个的组合。在某些实施例中,当处理β-丙内酯产物流以分离羰基化催化剂的一部分的步骤需要沉淀时,沉淀步骤包括添加催化剂(或催化剂的组分)难溶于其中的溶剂。在某些实施例中,添加如脂族烃、芳族烃或冷凝相CO_2的非极性溶剂以使催化剂沉淀。在某些实施例中,选自以下的溶剂添加到β-丙内酯产物流以使催化剂或催化剂组分沉淀:丁烷、戊烷、己烷、庚烷、辛烷、环戊烷、环己烷、萘烷、高级烷烃以及两种或大于两种烷烃的混合物。在某些实施例中,选自以下的溶剂添加到β-丙内酯产物流以使催化剂或催化剂组分沉淀:苯、甲苯、二甲苯、均三甲苯、氯苯、或其它经取代的苯化合物。在某些实施例中,超临界CO_2添加到β-丙内酯产物流以使催化剂或催化剂组分沉淀。在某些实施例中,当羰基化催化剂包括路易斯酸性金属错合物与金属羰基化合物的组合且非极性溶剂添加到β-丙内酯产物流时,这使得路易斯酸性金属错合物沉淀但在β-丙内酯产物流中留下催化剂

的羰基金属组分的至少一部分。在沈淀催化剂的实施例中，分离羰基化催化剂的步骤通常包含其它步骤，以将沉淀从产物流中移除，这类隔离步骤为所属领域中众所周知的，且可包含但不限于过滤、沉淀、离心、凝固和这些步骤中的两个或大于两个的组合。

[0388] 吸附

[0389] 在某些实施例中，羰基化催化剂再循环系统被配置成通过吸附羰基化催化剂或其组分来分离羰基化催化剂。在一些变化形式中，吸附可需要使用固体吸附材料来处理含有羰基化催化剂的产物流。合适的固体吸附材料可包含无机物质、活性碳、聚合物、树脂、或这些固体吸附材料中的两个或大于两个的任何组合。合适的无机吸附材料可包含硅胶、硅酸盐矿物、粘土、硅藻土、漂白土(Fuller's earth)、陶瓷、氧化锆、分子筛等等。合适的聚合物可包含聚苯乙烯、聚丙烯腈、聚酰亚胺、聚烯烃、聚酯、聚醚、聚碳酸酯、聚异氰酸酯等等。这类聚合物可任选地包含额外化学官能团，以增强其吸附羰基化催化剂或催化剂组分的能力。这类官能团可包含酸(例如，磺酸或羧酸)、配位基团(例如，胺、硫醇、膦、腈或硼基)和/或碱(例如，氨基或氮杂环)。在某些情况下，吸附材料(例如，不论无机或聚合)为酸性、碱性的，或已进行化学处理以增强催化剂的亲和性。在羰基化催化剂通过吸附而从含有羰基化催化剂的产物流中移除的实施例中，吸附剂可通过任何常规方法与产物流接触。这包含但不限于：使含有羰基化催化剂的产物流流过吸附剂固定床；使含有羰基化催化剂的产物流流过吸附剂流化床；使含有羰基化催化剂的产物流流过包括吸附材料的织物、网或过滤板；或使含有羰基化催化剂的产物流与吸附材料一起浆化(通常接着过滤、离心、沉淀等等，以将吸附剂从产物流中移除)。

[0390] 在β-丙内酯产物流流过吸附剂柱的实施例中，可需要提供与供应件并联的多个这类柱以将流体从一个柱切换到另一个。由此，当吸附剂的一个柱变得饱和催化剂时，所述柱可切换到流动路径外且流体可分流到新鲜柱——在某些实施例中，柱放置在流动路径中到切换到流动路径外的时间间隔对应于本文中所描述的方法中所述的“第一时间间隔”。当吸附剂用于将催化剂从β-丙内酯产物流中移除时，发明的方法将通常包含将催化剂或一或多种催化剂组分从吸附剂解吸附的步骤。这类解吸附方法为所属领域中众所周知的且将取决于吸附剂和催化剂的特性而变化。解吸附可包含使用极性溶剂或置换催化剂或催化剂组分的溶质来处理，或可包括试剂添加到吸附催化剂以使所述吸附催化剂再生或形成较少粘附到吸附固体的物种的反应性过程。

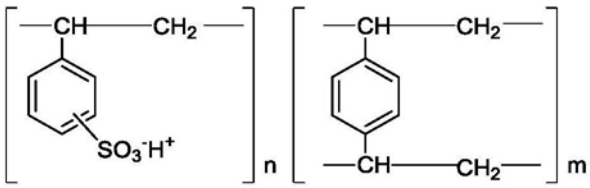
[0391] 离子交换

[0392] 在某些实施例中，羰基化催化剂再循环系统可被配置成通过羰基化催化剂或其组分的离子交换来分离羰基化催化剂。在某些实施例中，羰基化催化剂再循环系统被配置成通过使用离子交换材料处理β-丙内酯产物流来分离羰基化催化剂。离子交换材料可为例如阳离子、阴离子、两性、路易斯碱性、路易斯酸性的，或可包括螯合基。在某些实施例中，离子交换材料可为阳离子交换剂。在某些实施例中，阳离子交换材料上的官能团可选自：$-SO_3$、PO_3^{2-}、-COOH、$-C_6H_4OH$、-SH、$-AsO_3$或$-SeO_3$或这些官能团中的两个或大于两个的组合。在某些实施例中，阳离子交换材料上的官能团包括$-SO_3$。

[0393] 在某些实施例中，离子交换材料可为阴离子交换剂。在某些实施例中，阴离子交换材料上的官能团可选自：$-N^+$(烷基)$_3$、$-N^+(CH_3)_3$、$-N^+(CH_3)_2C_2H_4OH$、$-N^+(CH_3)_2C_2H_5$、$-P^+$(烷基)$_3$、$-P^+$(芳基)$_3$、$-P^+(C_4H_9)_3$，或$-P^+(Ph)_3$或这些官能团中的两个或大于两个的组合。在某些实

施例中，阴离子交换材料上的官能团包括-N^+(烷基)$_3$。在某些实施例中，阴离子交换材料上的官能团包括-P^+(烷基)$_3$。在某些实施例中，阴离子交换材料上的官能团包括-P^+(芳基)$_3$。

[0394] 在某些实施例中，羰基化催化剂再循环系统被配置成通过阴离子交换和阳离子交换来分离羰基化催化剂。在某些实施例中，当羰基化催化剂包括阳离子路易斯酸和阴离子金属羰基的组合时，单独地移除各阳离子路易斯酸和阴离子金属羰基，且方法包括使用阳离子交换物质处理β-丙内酯产物流以移除路易斯酸且使用阴离子交换物质处理以移除金属羰基。在某些实施例中，阴离子和阳离子交换同时进行。在某些实施例中，阴离子和阳离子交换相继地进行。在某些实施例中，首先执行阴离子交换，随后阳离子交换。在某些实施例中，首先执行阳离子交换，随后阴离子交换。在某些实施例中，可证实有机离子交换树脂被证实在包括有机离子用于包括有机离子交换树脂的分离步骤的离子交换材料为适用的。有机离子交换树脂一般拥有三维结构，矩阵。官能团可附接到结构，或直接地并入于聚合链中。矩阵可由线性聚合链构成，所述线性聚合链通过相对较短链彼此交联。借助于实例，在各种方面中，本公开包含使用包括与二乙烯基苯交联的磺化聚苯乙烯的离子交换材料：

[0395] 

[0396] 在各种方面中，离子交换材料可采取凝胶、或分布在珠粒上的凝胶树脂或其它载体基质的形式。在各种方面中，离子交换材料可采取大孔树脂的形式，所述大孔树脂具有由两个相组成的非均质结构、包括聚合物的凝胶区域和宏观的永久性孔。在本公开的各种实施例中，离子交换材料包括大孔网状树脂，所述大孔网状树脂为凝胶区域由多个珠粒微晶粒构成的额外大孔的树脂。离子交换材料可包括广泛多种形态和形式，包含孔隙度和其它表面特性中的变化形式。在各种方面中，材料可形成为但不限于：珠粒、球粒、球体、球状体、环、空心圆柱体、块状体、纤维、网、膜、纺织物。

[0397] 在各种方面中，珠粒大小可广泛分布，或可为极窄的所谓的单分散树脂。在催化剂通过离子交换从β-丙内酯产物流中移除的实施例中，离子交换材料可通过任何常规方法与产物流接触。这包含但不限于：使β-丙内酯产物流流过固体离子交换材料(即，呈珠粒、颗粒或其它粒子形式)的固定床；使β-丙内酯产物流流过吸附剂的流化床；使β-丙内酯产物流流过包括离子交换材料的织物、网或过滤板；或使β-丙内酯产物流与离子交换材料一起浆化(通常接着过滤、离心、沉淀等等，以将离子交换材料从产物流中移除)。在β-丙内酯产物流流过离子交换材料的填充柱的实施例中，可需要提供与供应件并联的多个这类柱以将流体从一个管柱周期性地切换到另一个。由此，当离子交换材料的一个柱变得饱和催化剂时，所述柱可切换到流动路径外且流体可分流到新鲜柱。在某些实施例中，柱放置在流动路径中到切换到流动路径外的时间间隔对应于本文中所描述的方法中所述的“第一时间间隔”。

[0398] 当离子交换材料用于将催化剂从β-丙内酯产物流中移除时，发明的方法将通常包含将催化剂或一或多种催化剂组分从离子交换材料中移除的后续步骤。这类移除方法为所属领域中众所周知的，且通常涉及使离子交换树脂与盐的浓溶液接触，所述盐的阴离子或阳离子将将催化剂组分从离子交换材料中置换。这个移除步骤的细节可取决于吸附剂和催化剂的特性而变化，但所属领域的技术人员已知合适的方法。

[0399] 离子液体

[0400] 在某些实施例中，羰基化催化剂再循环系统被配置成通过使用离子液体来分离羰基化催化剂。举例来说，在一些实施例中，羰基化催化剂再循环系统被配置成使用离子液体来分离羰基化催化剂，以形成包括离子液体相和β-丙内酯产物流的两相系统。催化剂(或其组分)的至少一部分萃取到离子液体相中，以使得催化剂的浓度在反应产物相中减小。随后移除包括羰基化催化剂的至少一部分的离子液体相，羰基化催化剂使用所属领域中已知的任何合适的方法来从离子液体相中隔离，且隔离的羰基化催化剂再循环回到羰基化反应器中。举例来说，在一些实施例中羰基化催化剂使用纳米过滤或沉淀来从离子液体相中隔离。有时，也可能使用离子交换树脂来进行这类分离。

[0401] 可使用所属领域中已知的任何合适的离子液体。在一些实施例中，使用离子液体的混合物。

[0402] 建构材料

[0403] 适合于羰基化催化剂再循环系统的建构材料可使用与例如所使用的膜相容的任何材料。在一些变化形式中，羰基化催化剂再循环系统具有惰性金属表面，例如以减小或消除聚合物成核位置。

[0404] 在其它变化形式中，羰基化催化剂再循环系统可使用弹性体密封，所述弹性体密封与环氧乙烷、一氧化碳和/或β-丙内酯相容且对大气几乎没有渗透性。实例可包含：卡乐瑞(Kalrez)6375、科拉兹(Chemraz)505、PTFE囊封的氟化橡胶(Viton)和PEEK。

[0405] 在其它变化形式中，羰基化催化剂再循环系统的外部部分的建构材料可与环境相容且不吸热，所述环境包含例如沙和盐水。另外，可采用安全联锁和安全操作参数。举例来说，羰基化催化剂再循环系统可被配置成在聚丙内酯生产系统/生产方法之前减缓聚丙内酯形成且/或避免催化剂分解(例如，通过在渗透物面或保留物面添加CO压力)。

[0406] 进入羰基化催化剂再循环系统的β-丙内酯产物流

[0407] 再次参考图1，来自β-丙内酯生产系统/生产方法的β-丙内酯产物流转移到羰基化催化剂再循环系统。在一些实施例中，β-丙内酯产物流包含至少约2000kg/hr bPL、至少约2500kg/hr bPL、至少约3000kg/hr bPL、至少约3500kg/hr bPL、至少约3638kg/hr bPL、至少约4000kg/hr bPL、至少约5000kg/hr bPL、至少约1000kg/hr bPL、至少约20000kg/hr bPL、至少约35000kg/hr bPL、至少约36380kg/hr bPL、或至少约40000kg/hr bPL。在一些实施例中，β-丙内酯产物流包含约2000kg/hr bPL、约2500kg/hr bPL、约3000kg/hr bPL、约3500kg/hr bPL、约3638kg/hr bPL、约4000kg/hr bPL、约5000kg/hr bPL、约1000kg/hr bPL、约20000kg/hr bPL、约35000kg/hr bPL、约36380kg/hr bPL、或约40000kg/hr bPL。在一些实施例中，β-丙内酯产物流包含在约2000kg/hr bPL与4000kg/hr bPL之间、约2500kg/hr bPL与4000kg/hr bPL之间、约3000kg/hr bPL与4000kg/hr bPL之间、约3500kg/hr bPL与4000kg/hr bPL之间、约3638kg/hr bPL与4000kg/hr bPL之间、约2000kg/hr bPL与40000kg/hr bPL之间、约2500kg/hr bPL与40000kg/hr bPL之间、约3000kg/hr bPL与40000kg/hr bPL之间、约3500kg/hr bPL与40000kg/hr bPL之间、约3638kg/hr bPL与40000kg/hr bPL之间、约4000kg/hr bPL与40000kg/hr bPL之间、约5000kg/hr bPL与40000kg/hr bPL之间、约1000kg/hr bPL与40000kg/hr bPL之间、约20000kg/hr bPL与40000kg/hr bPL之间、约35000kg/hr bPL与40000kg/hr bPL之间、约36380kg/hr bPL与

40000kg/hr bPL之间、或约40000kg/hr bPL与40000kg/hr bPL之间。在一些实施例中，β-丙内酯产物流包含至少约30kmol/hr bPL、至少约40kmol/hr bPL、至少约45kmol/hr bPL、至少约50kmol/hr bPL、至少约55kmol/hr bPL、至少约100kmol/hr bPL、至少约200kmol/hr bPL、至少约300kmol/hr bPL、至少约400kmol/hr bPL、至少约450kmol/hr bPL、至少约500kmol/hr bPL、或至少约550kmol/hr bPL。在一些实施例中，β-丙内酯产物流中的bPL的质量分数可为约0.1到0.4、约0.15到0.3、约0.18到0.25、约0.2到0.23、至少约0.15、至少约0.2、或至少约0.224。在一些实施例中，β-丙内酯产物流中的bPL的摩尔分数可为约0.1到0.4、约0.15到0.3、约0.18到0.25、约0.21到0.23、至少约0.15、至少约0.2、或至少约0.22。β-丙内酯产物流也可包含其它组分，所述其它组分包含：不反应的环氧乙烷(呈约0.005到0.05、约0.01到0.045、约0.04、至多约0.014、至多约0.02、或至多约0.05的质量分数)，不反应的一氧化碳(呈约0.0005到0.01、至多约0.01、或至多约0.02的质量分数)，乙醛(呈约0.0005到0.005、至多约0.005、或至多约0.01的质量分数)，丁二酸酐(呈约0.0005到0.005、至多约0.005、或至多约0.001的质量分数)，羰基化催化剂(呈约40到640kg/hr、300到640kg/hr、40到300kg/hr、40到64kg/hr、约45到60kg/hr、约50到60kg/hr、至多54.8kg/hr、至多60kg/hr、至多100kg/hr、至多300kg/hr、或至多约600kg/hr，或呈约0.001到0.005、约0.002到0.004、至多约0.003、或至多约0.004的质量分数)，以及剩余溶剂。在一些实施例中，β-丙内酯产物流包含羰基化催化剂组分(呈约40到640kg/hr、300到640kg/hr、40到300kg/hr、40到64kg/hr、约45到60kg/hr、约50到60kg/hr、至多54.8kg/hr、至多60kg/hr、至多100kg/hr、至多300kg/hr、或至多约600kg/hr，或呈约0.001到0.005、约0.002到0.004、至多约0.003、或至多约0.004的质量分数)。

[0408] 在一些实施例中，来自β-丙内酯生产系统/生产方法的β-丙内酯产物流可具有约40到100℃、约50到90℃、约65到75℃或约70℃的温度。在一些实施例中，β-丙内酯产物流可具有约1到15巴、约2到10巴、或约7巴的压力。

[0409] 离开羰基化催化剂再循环系统的β-丙内酯产物流

[0410] 在一些实施例中，离开羰基化催化剂再循环系统的β-丙内酯产物流包含至少约2000kg/hr bPL、至少约2500kg/hr bPL、至少约3000kg/hr bPL、至少约3100kg/hr bPL、至少约3200kg/hr bPL、至少约3500kg/hr bPL、至少约3638kg/hr bPL、至少约4000kg/hr bPL、至少约5000kg/hr bPL、至少约1000kg/hr bPL、至少约20000kg/hr bPL、或至少约35000kg/hr bPL。在一些实施例中，β-丙内酯产物流包含约2000kg/hr bPL、约2500kg/hr bPL、约3000kg/hr bPL、约3500kg/hr bPL、约3638kg/hr bPL、约4000kg/hr bPL、约5000kg/hr bPL、约1000kg/hr bPL、约20000kg/hr bPL、约35000kg/hr bPL、约36380kg/hr bPL、或约40000kg/hr bPL。在一些实施例中，离开羰基化催化剂再循环系统的β-丙内酯产物流包含在约2000kg/hr bPL与3500kg/hr bPL之间、约2500kg/hr bPL与3500kg/hr bPL之间、约3000kg/hr bPL与3500kg/hr bPL之间、约2000kg/hr bPL与35000kg/hr bPL之间、约2500kg/hr bPL与35000kg/hr bPL之间、约3000kg/hr bPL与35000kg/hr bPL之间、约3500kg/hr bPL与35000kg/hr bPL之间、约3638kg/hr bPL与35000kg/hr bPL之间、约4000kg/hr bPL与35000kg/hr bPL之间、约5000kg/hr bPL与35000kg/hr bPL之间、约1000kg/hr bPL与35000kg/hr bPL之间、或约20000kg/hr bPL与35000kg/hr bPL之间。在一些实施例中，隔离后的β-丙内酯产物流包含至少约30kmol/hr bPL、至少约35kmol/hr bPL、

至少约40kmol/hr bPL、至少约43kmol/hr bPL、至少约45kmol/hr bPL、至少约100kmol/hr bPL、至少约200kmol/hr bPL、至少约300kmol/hr bPL、或至少约350kmol/hr bPL。在一些实施例中，隔离后的β-丙内酯产物流中的bPL的质量分数可为约0.1到0.4、约0.15到0.3、约0.18到0.25、约0.2到0.24、至少约0.15、至少约0.2、或至少约0.225。在一些实施例中，隔离后的β-丙内酯产物流中的bPL的摩尔分数可为约0.1到0.4、约0.15到0.3、约0.18到0.25、约0.21到0.23、至少约0.15、至少约0.2、或至少约0.22。隔离后的β-丙内酯产物流也可包含其它组分，所述其它组分包含不反应的环氧乙烷(呈约0.005到0.05、约0.01到0.04、约0.044、至多约0.014、至多约0.02、或至多约0.05的质量分数)，不反应的一氧化碳(呈约0.0005到0.001、至多约0.001、或至多约0.002的质量分数)，乙醛(呈约0.0005到0.005、至多约0.005、或至多约0.01的质量分数)，丁二酸酐(呈约0.0005到0.0051、至多约0.005、或至多约0.01的质量分数)，羰基化催化剂(呈约0到50kg/hr、约0.5到20kg/hr、约1到15kg/hr、约0到5kg/hr、约0.5到2kg/hr、约1到1.5kg/hr、至多1.4kg/hr、至多约2kg/hr、至多10kg/hr、或至多20kg/hr)，以及剩余溶剂。在一些变化形式中，隔离后的β-丙内酯产物流可包含羰基化催化剂组分(呈约0到50kg/hr、约0.5到20kg/hr、约1到15kg/hr、约0到5kg/hr、约0.5到2kg/hr、约1到1.5kg/hr、至多1.4kg/hr、至多约2kg/hr、至多10kg/hr、或至多20kg/hr)。

[0411] 在一些实施例中，离开羰基化催化剂再循环系统的β-丙内酯产物流可具有约20到60℃、约30到50℃、约35到45℃、或约40℃的温度。在一些实施例中，离开羰基化催化剂再循环系统的β-丙内酯产物流可具有约1到15巴、约2到10巴、或约7巴的压力。

[0412] 羰基化催化剂再生和积聚

[0413] 羰基化催化剂可以除呈活性催化剂外的形式从催化剂再循环系统中回收。因此，参考图3，在一些变化形式中，保留物流324可需要通过一或多个额外步骤来进一步加工以使供用于β-丙内酯生产系统/生产方法的羰基化催化剂再生。

[0414] 另外，与β-丙内酯产物流分离的羰基化催化剂(或其组分)可通过一些时间间隔来积聚。积聚的催化剂(或组分)形成在羰基化过程中最终(完全或部分地)再使用的废催化剂批料。再使用催化剂的过程可与隔离催化剂的过程相同或可不同。同样地，所述催化剂可再用于相同过程但在另一天或在不同反应器中再使用。这与分离的催化剂处理为在相对较短周期内返回到反应器的反应过程内的流的方法相反。

[0415] 在某些实施例中，当羰基化催化剂包括阳离子路易斯酸与阴离子金属羰基的组合时，催化剂的阳离子路易斯酸部分从β-丙内酯产物流中采集而不采集相关的金属羰基。在某些实施例中，阳离子路易斯酸以具有除阴离子金属羰基外的相对离子的形式积聚。在这类实施例中，方法可包含在条件下处理阳离子路易斯酸的积聚批料以将和积聚的路易斯酸相关的非金属羰基阴离子与金属羰基阴离子交换的另一步骤。

[0416] 在某些实施例中，当羰基化催化剂包括阳离子路易斯酸与阴离子金属羰基的组合时，催化剂的金属羰基部分从β-丙内酯产物流中采集而不采集相关的路易斯酸。由此积聚的金属羰基可采集为阴离子金属羰基(例如通过阴离子交换)或可以另一形式积聚，所述另一形式如还原的金属物种、金属盐、中性金属羰基、混合的金属羰基错合物或某一其它形式。在这类实施例中，方法可包含处理积聚的物种以使催化活性金属羰基化合物再生的另一步骤。在完整羰基金属阴离子(例如通过阴离子交换树脂上采集来)积聚的情况下，这类步骤可包含复分解以将金属羰基阴离子从树脂中释放。这通常将需要使用另一阴离子(如

氯化钠)浸没树脂以置换金属羰基。金属羰基随后可作为其钠盐而获得且可用以根据已知催化剂合成程序产生活性催化剂。因此,在某些实施例中,本文中所描述的系统和方法包括将积聚的金属羰基阴离子从树脂中释放的其它步骤。在某些实施例中,这类步骤需要利用积聚金属羰基阴离子以通过将积聚的金属羰基与合适的路易斯酸组合而使活性催化剂再生的其它步骤。

[0417] 在某些实施例中,金属羰基可以除呈完整金属羰基阴离子外的形式积聚。举例来说,在CO不足的大气中,金属羰基可失去一或多个CO配位基以形成多核金属羰基物种、盐、或呈元素形式的沉淀物。在其它实施例中,强配位基可用以置换一或多个CO配位基且帮助将金属羰基采集为新错合物。众所周知,这类物种可用以通过在CO压力下处理而使明确界定的金属羰基化合物再生。因此,在某些实施例中,本文中所描述的系统和方法包含使来自非催化活性物质的催化活性金属羰基物种再生的其它步骤,所述非催化活性物质从β-丙内酯产物流中积聚。在某些实施例中,这类步骤需要在条件下处理来源于催化活性金属羰基化合物的积聚的残余物,以使适合于再使用的催化活性金属羰基再生。在某些实施例中,这类步骤包含在较高CO压力下处理积聚的残余物的步骤。在某些实施例中,方法包含在较高CO压力的条件下处理含钴残余物以将其转化成八羰基二钴的步骤,所属含钴残余物从β-丙内酯产物流中积聚。

[0418] 在某些实施例中,当与β-丙内酯产物流分离的催化剂的积聚包括回收单独回收的催化剂批料中的两种或大于两种单独催化剂组分的步骤时,可需要重组回收的催化剂组分的额外步骤以产生活性羰基化催化剂。在一些情况下,可直接地组合回收的催化剂组分,而在其它步骤中,一种或多种组分在组合步骤之前可需要如上文所描述加工。在某些实施例中,这类步骤需要复分解以将回收的阳离子路易斯酸与回收的金属羰基阴离子重组,所述回收的金属羰基阴离子如羰基钴酸盐。

[0419] 积聚批料所需的时间间隔取决于积聚模式以及将积聚的催化剂残余物转化成活性催化剂所需的任何方法的规模和经济情况。在一些实施例中,积聚催化剂或残余物的时间间隔约为数小时到数天,但可为数周。因此,在上文中所描述的方法中的任一种的某些实施例中,第一时间间隔在约1小时到约200小时的范围内。在某些实施例中,第一时间间隔为约2小时到约8小时、约4小时到约16小时、约12小时到约24小时、或约16小时到约36小时。在某些实施例中,第一时间间隔为约1天到约20天、约1天到约3天、约2天到约5天、约5天到约10天、或约10天到约20天。

[0420] 在这一时间期间,羰基化反应器可从催化剂存储器供应,所述催化剂随着积聚的催化剂(或催化剂残余物)的量在过程的后端增加而被消耗。可需要额外时间以加工积聚的催化剂或催化剂残余物来再制造活性催化剂。因此,在一些变化形式中,从积聚催化剂的第一时间间隔到羰基化反应器用含有催化剂的催化剂进料流供应的稍后时间已流逝某些倍数的第一时间间隔,所述催化剂来源于在第一时间间隔期间积聚的催化剂。在某些实施例中,第二时间间隔(在回收的催化剂供应到反应器的时间期间)与第一时间间隔(在积聚催化剂的时间期间)之间的时间长度约为第一时间间隔的长度的约1到约100倍。换句话说,如果第一时间间隔为10小时,那么第二时间间隔将在积聚步骤完成之后的约10小时到约2000小时出现。在某些实施例中,第二时间间隔与第一时间间隔之间的时间长度为第一时间间隔的长度的约1到约10倍。在某些实施例中,第二时间间隔与第一时间间隔之间的时间长度

为第一时间间隔的长度的约1到约3倍、约2到约5倍、约4到约10倍、约10到约50倍、约40到约80倍、或约50到约100倍。在某些实施例中，第二时间间隔与第一时间间隔之间的时间长度大于第一时间间隔的100倍。

[0421] 在预定速率下连续置换催化剂

[0422] 在某些变化形式中，羰基化催化剂再循环系统可被配置成连续地或间歇地将催化剂替代组分引入到羰基化反应器，所述催化剂替代组分不同于羰基化催化剂(例如，不同于羰基化催化剂源)且可包括选自由以下组成的群组的物种：路易斯酸、路易斯酸的前体、金属羰基和金属羰基的前体。

[0423] 在一些实施例中，催化剂替代组分包括路易斯酸。在一些实施例中，催化剂替代组分包括路易斯酸的前体。在一些实施例中，催化剂替代组分包括金属羰基。在一些实施例中，催化剂替代组分包括金属羰基的前体。

[0424] 在一些实施例中，催化剂替代组分以在一小时的时间段内使得羰基化反应的速率偏差小于10％的速率下引入。在一些实施例中，催化剂替代组分以在一小时的时间段内使得羰基化反应的速率偏差小于5％的速率下引入。

[0425] 在一些实施例中，催化剂替代组分添加到羰基化反应器的速率通过观测到羰基化反应速率降低的速率来确定。在一些实施例中，一或多种催化剂替代组分添加到羰基化反应器的的速率与观测到羰基化反应速率降低的速率成正比。

[0426] 在一些实施例中，一或多种催化剂替代组分以与相同观测到羰基化反应速率降低的速率连续地引入到羰基化反应器。在一些实施例中，一或多种催化剂替代组分间歇地引入到羰基化反应器，以产生匹配观测到羰基化反应速率降低的速率的平均速率。

[0427] 因此，如果观测到羰基化反应速率在时段过程上降低5％，那么催化剂替代组分可以存在于羰基化反应器中的5％的初始量的路易斯酸或金属羰基在相同时段上添加的这种速率连续地或间歇地添加。在一些实施例中，连续地添加催化剂替代组分。在一些实施例中，每小时添加催化剂替代组分。在一些实施例中，每30分钟添加催化剂替代组分。在一些实施例中，每15分钟添加催化剂替代组分。在一些实施例中，每10分钟添加催化剂替代组分。在一些实施例中，每5分钟添加催化剂替代组分。在一些实施例中，每分钟添加催化剂替代组分。

[0428] 所属领域的技术人员应了解，添加一或多种催化剂替代组分的间隔越短，将观测到总体羰基化反应速率中的偏差越小。然而，应认识到，这必须与其它考虑因素相平衡，所述其它考虑因素如进行多次添加的复杂度。

[0429] 再循环到BPL生产系统/生产方法

[0430] 在一些实施例中，羰基化催化剂和/或溶剂流可再循环到进料流或再循环到羰基化反应器。在一些实施例中，从β-丙内酯产物流再循环到羰化反应器或进料流的溶剂和/或催化剂的部分在约0％到约100％的范围内。在一些实施例中，从β-丙内酯产物流再循环到羰化反应器或进料流的溶剂和/或催化剂的部分为约100％、约90％、约80％、约70％、约60％、约50％、约40％、约30％、约20％、约10％、或约0％。在一些实施例中，再循环与溶剂相比不同百分比的催化剂，即，催化剂或溶剂组分的比例不需要相等。

[0431] BPL纯化系统(和溶剂再循环)

[0432] 在催化剂隔离系统之后，隔离后的羰基化流(即，隔离后的β-丙内酯产物流)可供

应到BPL纯化系统。当可需要高纯度bPL时，BPL纯化系统可在bPL进入聚合反应系统之前将所述bPL从低沸点杂质中分离到BPL纯化流中。在一些实施例中，BPL纯化流可具有至少约90wt％bPL、至少约95wt％bPL、至少约98wt％bPL、至少约99wt％bPL、至少约99.3wt％bPL、至少约99.5wt％bPL、至少约99.8wt％、或至少约99.9wt％。在一些实施例中，BPL纯化流可具有至多约1wt％溶剂、至多约0.5wt％溶剂、或至多约0.1wt％溶剂。在一些实施例中，BPL纯化系统也可产生溶剂再循环流。在一些实施例中，BPL纯化系统可将bPL与隔离后的羰基化流中的其它组分分离，所述其它组分如溶剂、不反应的环氧乙烷、不反应的一氧化碳、副反应产物乙醛、副反应产物丁二酸酐、和未在催化剂隔离系统中隔离的羰基化催化剂或其组分。将bPL与隔离后的羰基化流中的其它组分分离可通过所属领域的技术人员已知的各种方法来实现。

[0433] 羰基化催化剂组分可包含例如由催化剂的降解所产生的化合物、用于产生催化剂的化合物、金属或金属离子(其为催化剂的部分)、任何有机化合物(其为催化剂的部分)、金属羰基或金属错合物(其为催化剂的部分)。举例来说，在一些实施例中，羰基化催化剂组分是羰基钴酸盐、铝沙仑化合物、铝卟啉化合物、铝柳酰醋氨酚化合物、钴或钴离子、或铝或铝离子，或其任何组合。

[0434] 在一些实施例中，BPL纯化系统中的温度可为至多约150℃、至多约125℃、至多约115℃、至多约105℃、或至多约100℃。当bPL暴露于比100℃高的温度时，bPL可潜在地分解或被部分聚合。因此，bPL可在未暴露于约150℃、125℃、115℃、105℃、或100℃的温度的情况下纯化。

[0435] 在一些实施例中，分离通过采用β-丙内酯与羰基化产物流的其它组分之间的沸点差来进行，所述其它组分主要为溶剂。在一些实施例中，溶剂的沸点低于β-丙内酯的沸点。在一些实施例中，溶剂连同其它较轻组分(例如，环氧乙烷&乙醛)从BPL纯化进料中挥发(例如，蒸发)，留下来自BPL纯化进料的bPL、其它较重化合物(例如，催化剂和丁二酸酐)以及一些剩余的溶剂。在一些实施例中，这包含将BPL纯化进料暴露于减小的压力。在一些实施例中，这包含将BPL纯化进料暴露于增加的温度。在一些实施例中，这包含将BPL纯化进料暴露于减小的压力和增加的温度两个。

[0436] 在一些实施例中，选择压力以使得溶剂的沸点与大气压下的沸点相比减小约5℃。在一些实施例中，选择压力以使得溶剂的沸点与大气压下的沸点相比减小约10℃。在一些实施例中，选择压力以使得溶剂的沸点与大气压下的沸点相比减小约20℃。在一些实施例中，选择压力以使得溶剂的沸点与大气压下的沸点相比减小约50℃。

[0437] 在一些实施例中，增加的温度在所选择的压力下高于溶剂的沸点但低于β-丙内酯的沸点。在一些实施例中，温度低于β-丙内酯的沸点至少约20℃。在一些实施例中，温度低于β-丙内酯的沸点至少约30℃。在一些实施例中，温度低于β-丙内酯的沸点至少约50℃。

[0438] 在一些实施例中，减小的压力在约1托到约760托的范围内。在一些实施例中，压力在约1托到约400托的范围内。在一些实施例中，压力在约5托到约200托的范围内。在一些实施例中，压力在约10托到约100托的范围内。在一些实施例中，压力在约20托到约50托的范围内。在一些实施例中，压力为约50托、约100托、约150托、约200托、约250托、约300托、约400托、约500托、约600托、或约700托。

[0439] 在一些实施例中，分离步骤在低于约100托的压力和高于约120℃的温度下执行。

在一些实施例中，分离步骤在低于约50托的压力和高于约100℃的温度下执行。在一些实施例中，分离步骤在低于约50托的压力和高于约50℃的温度下执行。在一些实施例中，分离步骤在低于约50托的压力和高于约110℃的温度下执行。在一些实施例中，分离步骤在低于约50托的压力和高于约90℃的温度下执行。在一些实施例中，分离步骤在低于约20托的压力和高于约60℃的温度下执行。在一些实施例中，分离步骤在低于约10托的压力和高于约50℃的温度下执行。

[0440] 在一些实施例中，分离可以步骤序列实现，各步骤在独立的温度和压力下操作。举例来说，在一个实施例中，两个步骤可用于获得β-丙内酯的更有效分离，或单独的分离步骤可用于隔离某些反应副产物。在一些实施例中，当使用溶剂的混合物时，可需要多个分离步骤以单独地或作为群组移除特定溶剂，且有效隔离β-丙内酯。

[0441] 在某些实施例中，将β-丙内酯与BPL纯化进料分离在两个阶段中执行。在一些实施例中，过程包含移除BPL纯化进料的一或多种组分的基本的分离步骤，所述一或多种组分的沸点低于β-丙内酯产物的沸点。

[0442] 在一些实施例中，基本的分离步骤包含将BPL纯化进料分离成以下：包括环氧乙烷、溶剂、和bPL(以及潜在地一氧化碳、乙醛和/或bPL)的气流；以及包括β-丙内酯、羰基化催化剂(以及潜在地丁二酸酐和/或溶剂)的液流。在第二分离步骤中，液流进一步分离成：包括β-丙内酯的β-丙内酯流，包括溶剂的溶剂流，以及潜在地催化剂和丁二酸酐吹扫流。气流也可进一步分离成：包括溶剂的溶剂流，包括溶剂和环氧乙烷(以及潜在地乙醛)的较轻气流，以及包括bPL和溶剂的液体bPL流。液体bPL流可在分离液流之前与液流汇合，且形成第二分离步骤的组合进料。在一些实施例中，来自第二分离步骤的溶剂流和/或来自气流分离的溶剂流可形成溶剂再循环流，所述溶剂再循环流可供应到羰基化反应系统或可供应到溶剂储液器。

[0443] 在沸点低于β-丙内酯的沸点的一或多种溶剂存在的一些实施例中，较低沸点溶剂可在基本的分离步骤中从BPL纯化进料中挥发(例如，蒸发)，留下包括催化剂、β-丙内酯、其它溶剂(如果存在)和BPL纯化流中的其它化合物的混合物，所述BPL纯化流随后进一步处理以分离β-丙内酯流。

[0444] 在某些实施例中，当分离在两个阶段中执行时，第一分离步骤包括将反应流暴露于适度地减小的压力以产生气流和液流。在某些实施例中，当分离在两个阶段中执行时，气流可返回到羰基化步骤。

[0445] 在某些实施例中，将β-丙内酯与BPL纯化进料分离在三个阶段中执行。在第一分离步骤中，BPL纯化进料分离成以下：包括环氧乙烷、溶剂和bPL(以及潜在地一氧化碳和/或乙醛)的气流；以及包括溶剂、β-丙内酯和羰基化催化剂(以及潜在地丁二酸酐)的液流。在第二分离步骤中，气流分离成以下：包括溶剂的溶剂支流；包括环氧乙烷和溶剂(以及潜在地一氧化碳和/或乙醛)的较轻气流；以及包括溶剂和bPL的第二液流。在第三分离步骤中，第二液流和第一液流组合且分离成包括溶剂的气态溶剂流、包括bPL的纯化BPL流和潜在地催化剂和丁二酸酐吹扫流。在一些实施例中，溶剂支流和/或气态溶剂流可用作溶剂再循环流供用于羰基化反应系统或可存储在溶剂存储罐中。

[0446] 在某些实施例中，当分离在三个阶段中执行时，第一分离步骤包括将BPL纯化进料暴露于大气压。在某些实施例中，当分离在三个阶段中执行时，第二分离步骤包括将气流暴

露于大气压。在某些实施例中，当分离在三个阶段中执行时，第三分离步骤包括将气流暴露于真空或减小的压力。在某些实施例中，减小的压力在约0.05到0.25绝对巴之间。在某些实施例中，减小的压力在约0.1到0.2绝对巴之间或为约0.15绝对巴。

[0447] 在某些实施例中，将β-丙内酯与BPL纯化进料分离在四个阶段中执行。在第一分离步骤中，BPL纯化进料分离成以下：包括环氧乙烷、溶剂和bPL(以及潜在地一氧化碳和/或乙醛)的气流；以及包括溶剂、β-丙内酯和羰基化催化剂(以及潜在地丁二酸酐)的液流。在第二分离步骤中，气流分离成以下：包括溶剂的溶剂支流；包括环氧乙烷和溶剂(以及潜在地一氧化碳和/或乙醛)的较轻气流；以及包括溶剂和bPL的第二液流。在第三分离步骤中，第二液流和第一液流组合且分离成包括溶剂的气态溶剂流、包括bPL的纯化BPL流和潜在地催化剂和丁二酸酐吹扫流。在第四分离步骤中，较轻气流分离成包括溶剂的第三溶剂流和包括环氧乙烷(和潜在地一氧化碳和/或乙醛)的第二较轻气流。在一些实施例中，溶剂支流、气态溶剂流和/或第三溶剂流可用作溶剂再循环流供用于羰基化反应系统或可存储在溶剂存储罐中。

[0448] 在某些实施例中，当分离在四个阶段中执行时，第一分离步骤包括将BPL纯化进料暴露于大气压。在某些实施例中，当分离在四个阶段中执行时，第二分离步骤包括将气流暴露于大气压。在某些实施例中，当分离在四个阶段中执行时，第三分离步骤包括将组合的液流暴露于真空或减小的压力。在某些实施例中，减小的压力在约0.05到0.25绝对巴之间。在某些实施例中，减小的压力在约0.1到0.2绝对巴之间或为约0.15绝对巴。在某些实施例中，当分离在四个阶段中执行时，第四分离步骤包括将较轻气流暴露于大气压。

[0449] 在一些实施例中，BPL纯化系统可包含至少一个蒸馏柱以将bPL与隔离后的羰基化流中的其它组分分离。在一些实施例中，BPL纯化系统包含至少两个蒸馏柱。在一些实施例中，BPL纯化系统包含至少三个蒸馏柱。在一些实施例中，蒸馏柱中的至少一个为汽提柱(即，汽提器)。在一些实施例中，蒸馏柱中的至少一个为真空柱。在一些实施例中，BPL纯化系统可包含初始蒸发器，其中隔离后的羰基化流首先供应到BPL纯化系统中的蒸发器。蒸发器可执行隔离后的羰基化流中的溶剂与bPL之间的单次分离。蒸发器可减小后续蒸馏柱上的负载使所述蒸馏柱更小。在一些实施例中，蒸发器可通过大约在大气压和约100℃下蒸发隔离后的羰基化流中的溶剂来减小后续蒸馏柱的负载使所述后续蒸馏柱更小。

[0450] 图16绘示本文中所公开的BPL纯化系统的示范性实施例。

[0451] 进料流

[0452] 如图16中所描绘，在示范性系统的一些实施例中，BPL纯化系统1617的进料1616可为隔离后的羰基化产物流(即，隔离后的β-丙内酯产物流)。在其它实施例中，BPL纯化系统的进料可为羰基化产物流。在一些实施例中，BPL纯化系统的进料为至少约10000kg/hr、至少约11000kg/hr、至少约12000kg/hr、至少约13000kg/hr、至少约13777kg/hr、至少约20000kg/hr、至少约50000kg/hr、至少约100000kg/hr、至少约110000kg/hr、至少约120000kg/hr、至少约130000kg/hr、或至少约137770kg/hr。在一些实施例中，BPL纯化系统的进料为约10000kg/hr、约11000kg/hr、约12000kg/hr、约13000kg/hr、约13777kg/hr、约20000kg/hr、约50000kg/hr、约100000kg/hr、约110000kg/hr、约120000kg/hr、约130000kg/hr、或约137770kg/hr。在一些实施例中，BPL纯化系统的进料在约10000kg/hr与约13777kg/hr之间、约11000kg/hr与约13777kg/hr之间、约12000kg/hr与约13777kg/hr之间、约

13000kg/hr与约13777kg/hr之间、约10000kg/hr与137770kg/hr之间、约11000kg/hr与约137770kg/hr之间、约12000kg/hr与约137770kg/hr之间、约13000kg/hr与约137770kg/hr之间、约13777kg/hr与约137770kg/hr之间、约20000kg/hr与约137770kg/hr之间、约50000kg/hr与约137770kg/hr之间、约100000kg/hr与约137770kg/hr之间、约110000kg/hr与约137770kg/hr之间、约120000kg/hr与约137770kg/hr之间、或约130000kg/hr与约137770kg/hr之间。在一些实施例中，BPL纯化系统的进料具有约10到30、约15到28、约18到25、约20到25、约22到23之间、约22.5、或至少22.5的bPL wt％。在一些实施例中，BPL纯化系统的进料具有60到90、约65到85、约70到80、约72到78、约74到76之间、约75、约75.8、或至少约75的溶剂(例如，THF)wt％。在一些实施例中，BPL纯化系统的进料具有约0到0.2、约0.05到0.15之间、约0.1、或至多约0.2的CO wt％。在一些实施例中，BPL纯化系统的进料具有约0到0.2、约0.05到0.15之间、约0.1、至多约0.1、或至多约0.2的乙醛wt.％。在一些实施例中，BPL纯化系统的进料具有约0到0.2、约0.05到0.15之间、约0.1、至多约0.1、或至多约0.2的丁二酸酐wt.％。在一些实施例中，BPL纯化系统的进料具有约0到3、约0.5到2、约1到2之间、约1.4、至多约1.4、或至多约2的EO wt％。在一些实施例中，BPL纯化系统的进料具有痕量的羰基化催化剂。在一些实施例中，BPL纯化系统的进料具有痕量的羰基化催化剂组分。

[0453] 蒸发器

[0454] 在一些实施例中，BPL纯化系统的进料可供应到蒸发器1628。在一些实施例中，蒸发器可在至多约5绝对巴、至多约4绝对巴、至多约3绝对巴、至多约2绝对巴、至多约大气压(即，1绝对巴)或大约在大气压下操作。在一些实施例中，蒸发器可在约80到120℃之间、约90到100℃之间、约95到105℃之间、在约100℃、至多约100℃、至多约105℃、至多约110℃、或至多约120℃的温度下操作。在一些实施例中，蒸发器为闪蒸罐。再次参考图16，在示范性系统中，蒸发器1628可将进料分离成顶部物流1629和底部物流1630。顶部物流1629可主要包括THF以及低沸点组分(例如，CO、EO、乙醛)和少量bPL。在一些实施例中，顶部物流1629可具有至少约9000kg/hr、至少约10000kg/hr、至少约11000kg/hr、至少约11500kg/hr、或至少约12000kg/hr的质量流率。在一些实施例中，顶部物流1629可具有约75到95、约80到90、约85、约86.7、至少约75、至少约80、至少约85、或至少约90的溶剂(例如，THF)wt％。在一些实施例中，顶部物流1629可具有约0到20、约5到20、约8到15、约10、约11.5、至多约25、至多约20、至多约15、至多约11.5、至多约10、或至多约5的bPL wt％。在一些实施例中，顶部物流1629可具有约0到0.2、约0.05到0.15、约0.1、至多约0.2、或至多约0.1的一氧化碳wt％。在一些实施例中，顶部物流1629可具有约0到5、约0.5到3、约1到2、约1.6、至多5、至多3、至多2、至多1.6的环氧乙烷wt％。在一些实施例中，顶部物流1629可具有约0到0.4、约0.1到0.3、约0.2、至多约0.4、或至多约0.2的乙醛wt％。

[0455] 在一些实施例中，底部物流1630可具有至少约500kg/hr、至少约1000kg/hr、至少约1500kg/hr、至少约2000kg/hr、至少约2200kg/hr、至少约3000kg/hr、至少约4000kg/hr、至少约5000kg/hr、至少约10000kg/hr、至少约15000kg/hr、至少约20000kg/hr、至少约22000kg/hr、至少约30000kg/hr的质量流率。在一些实施例中，底部物流1630可具有在约500kg/hr与约3000kg/hr之间、约1000kg/hr与约3000kg/hr之间、约1500kg/hr与约3000kg/hr之间、约2000kg/hr与约3000kg/hr之间、约2200kg/hr与约3000kg/hr之间、约500kg/hr与约30000kg/hr之间、约1000kg/hr与约30000kg/hr之间、约1500kg/hr与约30000kg/hr之间、

约2000kg/hr与约30000kg/hr之间、约2200kg/hr与约30000kg/hr之间、约3000kg/hr与约30000kg/hr之间、约4000kg/hr与约30000kg/hr之间、约5000kg/hr与约30000kg/hr之间、约10000kg/hr与约30000kg/hr之间、约15000kg/hr与约30000kg/hr之间、约20000kg/hr与约30000kg/hr之间、约22000kg/hr与约30000kg/hr之间的质量流率。在一些实施例中，底部物流1630可具有约60到95、约65到90、约70到85、约75到85、约79.7、约80、至少约65、至少约70、至少约75、至少约79.7、至少约85的bPL wt％。在一些实施例中，底部物流1630可具有约5到40、约10到30、约15到25、约18到20、约19.2、约20、至多40、至多30、至多25、至多20、至多19.2、至多15、或至多10的溶剂wt％。在一些实施例中，底部物流1630可具有约0到0.4、约0.1到0.3、约0.2、至多约0.4、或至多约0.2的环氧乙烷wt％。在一些实施例中，底部物流1630可具有约0到2、约0.2到1.6、约0.4到1.2、约0.6到1、约0.7到0.9、至多约2、至多约1、至多约0.8的丁二酸酐wt％。在一些实施例中，底部物流1630可具有约0到0.2、约0.05到0.15、约0.1、至多约0.2、或至多约0.1的羰基化催化剂wt％。在一些实施例中，底部物流1630可具有约0到0.2、约0.05到0.15、约0.1、至多约0.2、或至多约0.1的羰基化催化剂组分wt％。

[0456] 溶剂纯化柱

[0457] 再次参考图16，在所描绘的示范性系统中，顶部物流1629可传送到溶剂纯化柱1631。溶剂纯化柱可以是蒸馏柱。在一些实施例中，溶剂纯化柱可为汽提柱或汽提器。在一些实施例中，溶剂纯化柱可在至多约5绝对巴、至多约4绝对巴、至多约3绝对巴、至多约2绝对巴、至多约大气压(即，1绝对巴)或大约在大气压下操作。在一些实施例中，蒸发器可在至多约100℃、至多约105℃、至多约110℃、或至多约120℃的温度下操作。在一些实施例中，顶部温度保持在约20到60℃、约30到50℃、约40到50℃、约44℃。在一些实施例中，溶剂纯化柱可防止bPL进入任何排气流。在一些实施例中，溶剂纯化柱可具有至少12个阶段，其中冷凝器作为阶段1。在一些实施例中，溶剂纯化柱可具有可产生支流的内部冷却器。在一些实施例中，溶剂纯化柱可具有在支流撤回口上的内部冷却器。在一些实施例中，内部冷却器可在柱中间的阶段之间。在一些实施例中，内部冷却器可在溶剂纯化柱的阶段5与阶段6之间。在一些实施例中，溶剂纯化柱可将顶部物流1629分离成顶部物流1632、底部物流1634和支流1633。顶部物流1632可包括低沸点组分(例如，EO、CO、乙醛)和大约一半溶剂。底部物流1634可主要包括bPL和溶剂。在一些实施例中，溶剂纯化柱可从底部物流1634中的顶部物流1629中回收至少90wt％、至少95wt％、至少98wt％、至少99wt％、或至少99.5wt％的bPL。

[0458] 在一些实施例中，顶部物流1632可具有至少200kg/hr、至少300kg/hr、至少400kg/hr、至少411kg/hr、至少500kg/hr、至少1000kg/hr、至少1500kg/hr、至少2000kg/hr、至少3000kg/hr、至少4000kg/hr、至少4110kg/hr、或至少5000kg/hr的质量流率。在一些实施例中，顶部物流1632可具有200kg/hr与500kg/hr之间、300kg/hr与500kg/hr之间、400kg/hr与500kg/hr之间、411kg/hr与500kg/hr之间、200kg/hr与5000kg/hr之间、300kg/hr与5000kg/hr之间、400kg/hr与5000kg/hr之间、411kg/hr与5000kg/hr之间的质量流率。在一些实施例中，顶部物流1632可具有约30到70、约40到60、约45到55、约50到55、约50、约53.9、至多75、至多65、至多60、至多55、至多53.9、至多50、至多45的溶剂(例如，THF)wt％。在一些实施例中，顶部物流1632可具有约20到60、约30到50、约35到45、约37到43、约40.6、至少约20、至少约25、至少约30、至少约35、至少约40、至少约40.6、至少约45或至少约50的环氧乙烷wt％。在一些实施例中，顶部物流1632可具有约0到5、约0.5到3、约1到2、约1.5到2、约1.7、至多约

5、至多约3、至多约2、至多约1.7、至多约1的一氧化碳wt％。在一些实施例中，顶部物流1632可具有约0到10、约1到7、约2到5、约3到4.5、约3.5到4、约3.8、至多约10、至多约7、至多约5、至多约4、至多约3.8、至多约3的乙醛wt％。

[0459] 在一些实施例中，底部物流1634可具有至少约1000kg/hr、至少约1200kg/hr、至少约1400kg/hr、至少约1600kg/hr、至少约1643kg/hr、至少约1800kg/hr、至少约4000kg/hr、至少约7500kg/hr、至少约10000kg/hr、至少约12000kg/hr、至少约14000kg/hr、至少约16000kg/hr、至少约16430kg/hr、或至少约18000kg/hr的质量流率。在一些实施例中，底部物流1634可具有约1000kg/hr、约1200kg/hr、约1400kg/hr、约1600kg/hr、约1643kg/hr、约1800kg/hr、约4000kg/hr、约7500kg/hr、约10000kg/hr、约12000kg/hr、约14000kg/hr、约16000kg/hr、约16430kg/hr、或约18000kg/hr的质量流率。在一些实施例中，底部物流1634可具有1000kg/hr与1800kg/hr之间、1200kg/hr与1800kg/hr之间、1400kg/hr与1800kg/hr之间、1600kg/hr与1800kg/hr之间、1643kg/hr与1800kg/hr之间、1000kg/hr与18000kg/hr之间、1200kg/hr与18000kg/hr之间、14000kg/hr与18000kg/hr之间、16000kg/hr与18000kg/hr之间、1643kg/hr与18000kg/hr之间、4000kg/hr与18000kg/hr之间、10000kg/hr与18000kg/hr之间、或16000kg/hr与18000kg/hr之间的质量流率。在一些实施例中，底部物流1634可具有约60到95、约70到90、约75到85、约80、约80.4、至少60、至少70、至少75、至少80、至少80.4、至少85、至少90、或至少95的bPL wt％。在一些实施例中，底部物流1634可具有约5到40、约10到30、约15到25、约20、约19.5、至多40、至多30、至多25、至多20、至多19.5、至多15、或至多10的溶剂wt％。在一些实施例中，底部物流1634可具有约0到0.4、约0.1到0.3、约0.2、至多约0.4、或至多约0.2的环氧乙烷wt％。

[0460] 在一些实施例中，支流1633可具有至少约6000kg/hr、至少约7000kg/hr、至少约8000kg/hr、至少约9000kg/hr、至少约9500kg/hr、至少约9508kg/hr、至少约10000kg/hr、至少约20000kg/hr、至少约40000kg/hr、至少约60000kg/hr、至少约70000kg/hr、至少约80000kg/hr、至少约90000kg/hr、至少约95000kg/hr、至少约95080kg/hr、或至少约100000kg/hr的质量流率。在一些实施例中，支流1633可具有约6000kg/hr、约7000kg/hr、约8000kg/hr、约9000kg/hr、约9500kg/hr、约9508kg/hr、约10000kg/hr、约20000kg/hr、约40000kg/hr、约60000kg/hr、约70000kg/hr、约80000kg/hr、约90000kg/hr、约95000kg/hr、约95080kg/hr、或约100000kg/hr的质量流率。在一些实施例中，支流1633可具有6000kg/hr与10000kg/hr之间、7000kg/hr与10000kg/hr之间、8000kg/hr与10000kg/hr之间、9000kg/hr与10000kg/hr之间、9500kg/hr与10000kg/hr之间、9508kg/hr与10000kg/hr之间、6000kg/hr与100000kg/hr之间、10000kg/hr与100000kg/hr之间、20000kg/hr与100000kg/hr之间、40000kg/hr与100000kg/hr之间、60000kg/hr与100000kg/hr之间、70000kg/hr与100000kg/hr之间、80000kg/hr与100000kg/hr之间、或90000kg/hr与100000kg/hr之间的质量流率。在一些实施例中，支流1633可具有至少95、至少98、至少99、至少99.7的溶剂wt％。在一些实施例中，支流1633可具有约0到0.4、约0.1到0.3、约0.2、至多约0.4、或至多约0.2的环氧乙烷wt.％。在一些实施例中，支流1633可具有约0到0.2、约0.05到0.15、约0.1、至多约0.1、或至多约0.2的bPL wt％。

[0461] BPL纯化柱

[0462] 底部物流1630和底部物流1634可组合且传送到BPL纯化柱1635。BPL纯化柱可为蒸

馏柱。在一些实施例中，BPL纯化柱可为真空柱或在减压下操作的柱。在一些实施例中，BPL纯化柱的操作压力可小于大气压(1绝对巴)，小于约0.5绝对巴，小于约0.25绝对巴，小于0.2绝对巴，小于0.15绝对巴、或约0.15绝对巴。在一些实施例中，BPL纯化柱可包含再沸器，所述再沸器可保持在至多约120℃、至多约110℃、至多约100℃、或约100℃。在一些实施例中，顶部温度保持在约5到30℃、约10到20℃、约12到16℃、约14℃。

[0463] 在一些实施例中，BPL纯化柱可将组合的底部物流1630和1634分离成顶部物流1636和底部物流1618(即，BPL纯化流1618)。底部物流1618可为具有极少溶剂的大体上纯净bPL。在一些实施例中，底部物流1618也可包含一些较重组分，如残余羰基化催化剂和丁二酸酐。羰基化催化剂可被视为非挥发性且可积聚于BPL纯化柱的贮罐中。当催化剂wt％达到预定义值(例如，至少1wt％、2wt％、3wt％、4wt％、或5wt％)时，积聚的催化剂可通过吹扫贮罐来周期性地移除。与羰基化催化剂相比，丁二酸酐可具有一些挥发性且如果，积聚于贮罐中，那么所述丁二酸酐可产生再沸器中的非所要的沸腾温度的升高。在一些实施例中，丁二酸酐也可积聚于贮罐中且可以与可吹扫积聚的催化剂相同的方式来吹扫。在一些实施例中，顶部物流1636可具有约至少约500kg/hr、至少约600kg/hr、至少约700kg/hr、至少约750kg/hr、至少约800kg/hr、或至少约850kg/hr的质量流率。在一些实施例中，顶部物流1636可具有至少约95、至少约98、至少约99、至少约99.1或至少约99.5的溶剂wt％。在一些实施例中，顶部物流1636可具有约0到3、约0.2到2、约0.2到1.5、约0.5到1、约0.8、至多约3、至多约2、至多约1、至多约0.8、至多约0.5的环氧乙烷wt％。在一些实施例中，顶部物流1638可具有约0到0.2、约0.05到0.15、约0.1、至多约0.1、或至多约0.2的乙醛wt％。

[0464] 在一些实施例中，底部物流1618可具有至少约1000kg/hr、至少约2000kg/hr、至少约2500kg/hr、至少约3000kg/hr、至少约3100kg/hr、至少约3500kg/hr、至少约4000kg/hr、至少约5000kg/hr、至少约1000kg/hr、至少约20000kg/hr、至少约35000kg/hr、至少约36380kg/hr、或至少约40000kg/hr的质量流率。在一些实施例中，底部物流1618可具有约2000kg/hr、约2500kg/hr、约3000kg/hr、约3500kg/hr、约3638kg/hr、约4000kg/hr、约5000kg/hr、约1000kg/hr、约20000kg/hr、约35000kg/hr、约36380kg/hr、或约40000kg/hr的质量流率。在一些实施例中，底部物流1618可具有1000kg/hr与4000kg/hr之间、或1000kg/hr与40000kg/hr之间的质量流率。在一些实施例中，底部物流1618可具有至少约95、至少约98、至少约99、至少约99.3、或至少约99.5的bPL wt％。在一些实施例中，底部物流1618可具有约0到0.2、约0.05到0.15、约0.1、至多约0.1、或至多约0.2的溶剂wt.％。在一些实施例中，底部物流1618可具有约0到3、约0.1到2、约0.2到1、约0.5到1、约0.6、至多约3、至多约2、至多约1、至多约0.6、至多约0.5的丁二酸酐wt％。在一些实施例中，底部物流1618可具有痕量的羰基化催化剂。在一些实施例中，BPL纯化柱可对底部物流1618中的羰基化催化剂和/或丁二酸酐进行吹扫。在一些实施例中，吹扫可为阀门。

[0465] 轻气体柱

[0466] 可将顶部物流1632传送到待分离成顶部物流1639和底部物流1638的轻气体管柱1637。轻气体柱可以是蒸馏柱。在一些实施例中，轻气体柱可在最多约5巴、最多约4巴、最多约3巴、最多约2巴、最多约常压(即1巴)或约在常压下操作。在一些实施例中，轻气体柱可包含部分冷凝器。在一些实施例中，部分冷凝器在约0到20℃、约5到15℃、约10到15℃、约10到13℃下的温度下操作。在一些实施例中，维持在轻气体柱的底部的温度为约20到70℃、约40

到60℃、约45到55℃或约50℃。在一些实施例中，维持在轻气体柱中的顶部温度可为约-10到10℃、约-5到5℃、约-2到3℃或约1℃。顶部物流1639主要可包括在羰基化反应系统中所产生的乙醛以及低沸点环氧乙烷。在一些实施例中，可排放(例如焚化炉、燃烧柱等)顶部物流1639，因此乙醛并不积聚在整个生产系统/生产方法中。

[0467] 在一些实施例中，顶部物流1639可具有约50kg/hr、约100kg/hr、约150kg/hr、约175kg/hr、约200kg/hr、约250kg/hr、至少500kg/hr、至少1000kg/hr、至少1500kg/hr、至少2000kg/hr或至少2500kg/hr的质量流率。在一些实施例中，顶部物流1639可具有介于50kg/hr与250kg/hr之间、介于100kg/hr与250kg/hr之间、介于200kg/hr与250kg/hr之间或介于50kg/hr与2000kg/hr之间的质量流率。在一些实施例中，顶部物流1639可具有至少约70、至少约75、至少约80、至少约85、至少约89.5、至少约90或至少约95的环氧乙烷wt％。在一些实施例中，顶部物流1639可具有约0到15、约1到10、约2到8、约6.1、最多约15、最多约10、最多约6.1、最多约5或最多约2的乙醛wt％。在一些实施例中，顶部物流1639可具有约0到12、约1到10、约2到6、约4.10、最多约12、最多约10、最多约6、最多约5、最多约4.1或最多约2的一氧化碳wt％。在一些实施例中，顶部物流1639可具有约0到2、约0.1到1、约0.2到0.6、约0.4、最多约2、最多约1、最多约0.5、最多约0.4或最多约0.2的溶剂wt.％。

[0468] 在一些实施例中，底部物流1638可具有约50kg/hr、约150kg/hr、约200kg/hr、约235kg/hr、约250kg/hr、约300kg/hr或约350kg/hr的质量流率。在一些实施例中，底部物流1638具有至少约75、至少约80、至少约85、至少约90、至少约93.9、至少约95、至少约98或至少约99的溶剂wt％。在一些实施例中，底部物流1638具有约0到12、约1到10、约2到6、约4、最多约12、最多约10、最多约8、最多约5、最多约4或最多约2的环氧乙烷wt％。在一些实施例中，底部物流1638具有约0到10、约0.5到5、约1到4、约1到3、约2.2、最多约10、最多约5、最多约2.2、最多约2、最多约1的乙醛wt％。

[0469] 溶剂再循环流

[0470] 在一些实施例中，侧流1633、底部物流1638、顶部物流1636或其组合可形成溶剂再循环流1623。在一些实施例中，可将侧流1633、底部物流1638以及顶部物流1636进行组合以形成溶剂再循环流1623。在一些实施例中，侧流1633、底部物流1638和/或顶部物流1636可传送到溶剂再循环罐或存储仓。在一些实施例中，将溶剂再循环流供应回到羰基化反应系统。在一些实施例中，供应到羰基化反应系统的溶剂再循环流来自溶剂再循环罐或存储仓。在一些实施例中，进入和/或排出溶剂再循环罐或存储仓的溶剂流可(例如)通过使所述流穿过吸收器以从所述流中去除潜在的氧和/或水分来纯化。在一些实施例中，溶剂再循环罐或存储仓可配备有传感器以确定存储罐中的水和/或氧含量。

[0471] 优选蒸馏系统

[0472] 在优选实施例中，蒸馏子系统由3个蒸馏柱组成：(1)轻物质去除柱、(2)THF溶剂回收柱以及(3)bPL纯化柱。

[0473] 1.轻物质去除柱

[0474] 这个柱的目的是回收环氧乙烷(EO)以用于再循环回到羰基化反应器，以及分离如乙醛(ACH)的低沸点杂质。来自此柱的馏出物流可含有THF、EO、ACH或仅EO和ACH。这个柱接收来自羰基化催化剂回收区域的渗透流且以高度优选的形式具有含有代表性组成物的以下组分：THF(约75.2wt％)、bPL(约20.5wt％)、环氧乙烷(约4.1wt％)、乙醛(约0.07wt％)、

丁二酸酐(约0.02wt%)、痕量的低沸点和高沸点杂质,且将痕量残余羰基化催化剂供应到轻物质去除蒸馏柱。所述蒸馏柱在约1.3巴的压力下操作(柱在常压或略微高于常压下操作)。再沸器温度维持在105℃下或更低。将主要由THF(约93.4wt%)、EO(约6.5wt%)、ACH(0.1wt%)以及痕量的低沸点杂质组成的轻物质柱馏出物流供应回到羰化反应器或到任选ACH去除系统。轻物质柱以高度优选的形式产生主要由bPL(约54.9wt%)、THF(约45.0wt%)、丁二酸酐(约0.05wt%)、痕量的低沸点和高沸点杂质组成的底部物流,且将痕量残余羰基化催化剂和高沸点杂质向前供应到THF溶剂回收柱(2)。

[0475] 在一些实施例中,轻物质去除柱可以此方式操作使得馏出物流仅由环氧乙烷和乙醛组成且全部THF从具有底部物流的柱中排出。如果轻物质去除柱以这种配置操作,那么馏出物基本上由以下组成:EO(约98.8wt%)、ACH(约1.2wt%)以及痕量的低沸点杂质。以这种柱配置的底部物流基本上由以下组成:THF(约78.5wt%)、bPL(约21.5wt%)、SAH(约0.02wt%)、痕量的残余羰基化催化剂、痕量的低沸点和高沸点杂质。

[0476] 积聚在羰基化/蒸馏系统内的乙醛可通过对馏出物流实施少量吹扫或使用如分子筛(非限制性实例为分子筛3A、4A、5A、13X等)的吸收剂从馏出物流中去除来避免。任选地,使用蒸馏或萃取蒸馏来使ACH与EO分离。

[0477] 2.THF溶剂回收柱

[0478] 这个柱的目的是回收THF溶剂以用于再循环回到羰化反应器。由于bPL的高沸点(在常压下162℃),因此这个柱在低于常压的压力下操作以将再沸器温度限制在105℃以下且避免bPL的自动聚合。来自这个柱的馏出物流含有基本上纯净的THF且这个柱的底部物流含有bPL、SAH、残余羰基化催化剂以及痕量的高沸点杂质。

[0479] 将含有THF、bPL、SAH、残余羰基化催化剂以及痕量的低沸点和高沸点杂质的轻物质柱底部物流供应到THF溶剂回收蒸馏柱(此物流的组成物呈现在以上部分中)。任选地,可将THF溶剂补充流供应到这个柱——这允许将O_2、H_2O以及BHT抑制剂从补充THF中去除。

[0480] 蒸馏柱在约100托的绝对压力下操作(柱在真空下操作),且再沸器温度维持在105℃下或更低。所述柱设计成最小化浸入到柱中的空气,简化对来自下游单元操作中的再循环THF溶剂流的O_2和H_2O杂质的去除。

[0481] 将来自这个柱中由含有痕量的低沸点和高沸点杂质的基本上纯净的THF(纯度大于99.9wt%)组成的馏出物流再循环回到羰化反应器。任选地且在其再循环之前,此物流可穿过纯化系统以用于去除如O_2和H_2O的杂质。这些杂质可以如吸收、吸附、萃取蒸馏、共沸蒸馏等本领域中已知的任何手段来去除。

[0482] 底部物流由bPL(约99.8wt%)、SAH(约0.1wt%)、少量的残余羰基化催化剂以及痕量的低沸点和高沸点杂质组成。将此物流向前供应到bPL纯化柱。

[0483] 3.bPL纯化柱

[0484] 这个柱的目的是回收已纯化的bPL以用于PPL(聚丙内酯)的后续产生。由于bPL的高沸点(在常压下162℃),因此这个柱在低于常压的压力下操作以将再沸器温度限制在105℃以下且避免bPL的自动聚合。来自这个柱的馏出物流含有基本上纯净的bPL。这个柱的底部物流含有残余bPL、SAH、残余羰基化催化剂以及痕量的高沸点杂质。将已纯化的bPL物流向前供应到聚合反应器且传送底部物流以用于安置或回收残余bPL和SAH。将来自THF回收柱中含有bPL(约99.8wt%)、SAH(约0.1wt%)、残余羰基化催化剂以及痕量的低沸点和高沸

点杂质的底部物流供应到bPL纯化柱。

[0485] bPL纯化柱以优选形式在约60托的绝对压力下操作(柱在真空下操作)且再沸器温度维持在105℃下或更低。将由含有痕量的低沸点和高沸点杂质的基本上纯净的bPL(纯度大于99.9wt%)组成的馏出物流向前供应到bPL聚合反应器。

[0486] 这个柱的底部物流由bPL(约88.9wt%)、SAH(约9.7wt%)、羰基化催化剂(约1.4wt%)以及痕量高沸点杂质组成。在这个底部物流中选择一定量的bPL以避免SAH在低于其119℃的熔点的温度下结晶且将再沸器温度限制到105℃以下。

[0487] 聚丙内酯生产系统/生产方法

[0488] 参考图2,描绘聚丙内酯生产系统/生产方法与其它单元操作(如β-丙内酯纯化系统、离子去除单元)的关系,以及冰丙烯酸生产系统/生产方法。

[0489] β-丙内酯纯化系统202被配置成将β-丙内酯产物物流供应到聚丙内酯生产系统/生产方法210中。均相催化剂递送系统204被配置成将均相聚合催化剂供应到聚丙内酯生产系统/生产方法210的聚合反应器中。聚丙内酯生产系统/生产方法210被配置成使β丙内酯聚合以产生聚丙内酯。根据所选择的聚合反应器的类型和这类反应器的配置,以及操作条件(例如操作温度、操作压力和驻留时间)和所使用聚合催化剂的选择,可控制β-丙内酯的转化的程度。在一些变化形式中,操作温度是反应器的内容物的平均温度。

[0490] 在一些变化形式中,实现β-丙内酯到聚丙内酯的部分转化,且bPL再循环单元220被配置成将未反应的β-丙内酯的至少部分再循环到聚丙内酯生产系统/生产方法210。在其它变化形式中,实现β-丙内酯到聚丙内酯的完全转化。将由聚丙内酯生产系统/生产方法210所产生的聚丙内酯产物流供应到被配置成从聚丙内酯产生冰丙烯酸的冰丙烯酸生产系统/生产方法250。存在离子去除单元230和260以去除阳离子和/或阴离子羰基化催化剂物种,所述催化剂物种可从β-丙内酯生产系统/生产方法(未在图2中描绘)中的上游羰基化反应中夹带过来。举例来说,当羰基化催化剂是钴铝化合物时,可由离子去除单元230和260来去除钴和铝的物种。由离子去除单元所分离的离子物种可使用单元270来安置,或在单元280中再生以产生可再循环到β-丙内酯生产系统/生产方法中的活性羰基化催化剂。

[0491] 在一些变化形式中,单元240被配置成从聚丙内酯生产系统/生产方法210中接收聚丙内酯产物物流(例如呈液体形式),且被配置成对聚丙内酯产物物流进行粒化、挤塑、剥落或造粒。

[0492] 然而,应理解,图2提供一个这些单元操作的示范性配置。在其它变化形式中,可添加、组合或忽略图2中所描绘的单元操作中的一或多个,且也可改变所述单元操作的次序。

[0493] 再次参考图1,聚丙内酯生产系统/生产方法被配置成通过在聚合催化剂的存在下使β-丙内酯聚合来产生聚丙内酯。尽管图1描绘用于使β-丙内酯聚合以产生聚丙内酯的单个推流式反应器的使用,然而可采用其它反应器类型和反应器配置。

[0494] 在一些实施例中,聚丙内酯生产系统/生产方法包含β-丙内酯、聚合引发剂或催化剂源以及至少一个聚合反应器。

[0495] BPL源

[0496] 再次参考图6到13,进入聚丙内酯生产系统/生产方法的bPL可以是来自bPL纯化组列的已纯化bPL或来自聚合反应器的再循环bPL,或其一组合。

[0497] 在一些实施例中,聚合方法的入口可包含至少约2000kg/hr bPL、至少约2500kg/

hrbPL、至少约3000kg/hr bPL、至少约3086kg/hr bPL、至少约3500kg/hr bPL、至少约3638kg/hr bPL、至少约4000kg/hr bPL、至少约5000kg/hr bPL、至少约1000kg/hr bPL、至少约20000kg/hr bPL或至少约35000kg/hr bPL。在一些实施例中，聚合方法的入口可包含约2000kg/hr bPL、约2500kg/hr bPL、约3000kg/hr bPL、约3500kg/hr bPL、约3638kg/hr bPL、约4000kg/hr bPL、约5000kg/hr bPL、约1000kg/hr bPL、约20000kg/hr bPL或约35000kg/hr bPL。在一些实施例中，聚合方法的入口可包含介于约2000kg/hr bPL与约3500kg/hr bPL之间、介于约2500kg/hr bPL与约3500kg/hr bPL之间、介于约3000kg/hr bPL与约3500kg/hr bPL之间、介于约2000kg/hr bPL与约35000kg/hr bPL之间、介于约2500kg/hr bPL与约35000kg/hr bPL之间或介于约3000kg/hr bPL与约35000kg/hr bPL之间。在一些实施例中，聚合方法的入口可包含至少约25kmol/hr bPL、至少约30kmol/hr bPL、至少约40kmol/hr bPL、至少约42kmol/hr bPL或至少约50kmol/hr bPL。在一些实施例中，bPL在聚合方法的入口中的的质量分数可以是至少约0.90、至少约0.95、至少约0.98、至少约0.99以及至少约0.993。在一些实施例中，bPL在聚合方法的入口中的的摩尔分数可以是至少约0.90、至少约0.95、至少约0.98、至少约0.99以及至少约0.995。进入聚合方法的产物物流的其余部分可包含如丁二酸酐(以最多约0.015、最多约0.01或最多约0.004的摩尔分数)的副反应产物和剩余溶剂(例如THF)以及剩余的羰基化催化剂(以最多约1000ppm)。在一些变化形式中，进入聚合方法的产物物流的其余部分可包含羰基化催化剂组分(以最多约1000ppm)。

[0498] 在一些变化形式中，进入聚合方法的产物物流进一步包括其它化合物，如羰基化催化剂或其组分。举例来说，在一些实施例中，产物物流进一步包括来自羰基化催化剂中的钴或铝，或其一组合。

[0499] 羰基化催化剂组分可包含(例如)由催化剂的降解所产生的化合物、用于产生催化剂的化合物、金属或金属离子(其为催化剂的部分)、有机化合物(其为催化剂的部分)、羰基金属或金属错合物(其为催化剂的部分)。举例来说，在一些实施例中，羰基化催化剂组分是羰基钴酸盐、铝沙仑化合物(aluminum salen compounds)、铝卟啉化合物、铝柳酰醋氨酚化合物、钴或钴离子，或铝或铝离子，或其任何组合。

[0500] 在某些变化形式中，进入聚合方法的产物物流包括钴。在一些实施例中，钴是Co^{-1}、Co、Co^{+}、Co^{2+}或Co^{3+}，或其一组合。在一些实施例中，产物物流具有介于0.001mM与1mM、0.001mM与0.5mM之间、介于0.001mM与0.05mM之间、介于0.005mM与0.02mM之间或介于0.007mM与0.015mM之间的钴浓度。

[0501] 在某些变化形式中，进入聚合方法的产物物流包括铝。在一些实施例中，产物物流中铝的浓度介于0.001mM与1mM、0.001mM与0.5mM之间、介于0.001mM与0.05mM之间、介于0.005mM与0.02mM之间或介于0.007mM与0.015mM之间。在某些变化形式中，进入聚合方法的产物物流含有少于1ppm的钴和少于1ppm的铝。

[0502] 在一些实施例中，聚合方法的入口也可包含聚合催化剂，例如，在所述聚合反应是均相聚合反应的情况下。进入聚合方法的产物物流可以是来自BPL纯化系统(例如BPL蒸馏系统)的重质(即底部残留物)物流。在一些实施例中，进入聚合方法的产物物流可具有介于约30到120℃之间、介于约50到110℃之间或约70℃的温度。在一些实施例中，进入聚合方法的产物物流可处在至少约0.05巴、至少约0.1巴、至少约5巴、至少约10巴、至少约15巴或至

少约20巴的压力下。在一些实施例中，进入聚合方法的产物物流介于0.05巴与20巴之间、介于0.1巴与20巴之间、介于5巴与15巴之间或介于10巴与20巴之间。

[0503] 在一些变化形式中，进入聚合方法的bPL供应速率与聚合引发剂供应速率的摩尔比从500到20,000、从1,000到10,000、从2,000到9,000、从3,000到8,000、从5,000到7,000、从1,000到110,000、从5,000到110,000、从25,000到110,000、从50,000到110,000或从75,000到110,000。在一个实施例中，进入聚合方法的bPL供应速率与聚合催化剂供应速率的摩尔比从1,000到9,000。

[0504] 在一些变化形式中，来自bPL纯化过程的bPL和从聚合方法中再循环的bPL两者都进入聚合方法。在某些实施例中，再循环的bPL与来自bPL纯化过程的bPL的重量比从0到0.01:0.99、从0.4:0.6到0.1:0.9、从0.5:0.5到0.15:0.85、从0.35:0.65到0.1:0.9或从0.25:0.75到0.15:0.85。

[0505] 其它供应源

[0506] 聚合方法可进一步包含其它供应源。举例来说，在一种变化形式中，聚合系统进一步包含聚合引发剂源，且反应器被配置成从这类源接收聚合引发剂。在一些变化形式中，聚合引发剂是亲核试剂。

[0507] 聚合条件

[0508] 在某些实施例中，bPL到PPL的转化以连续流形式来执行。在某些实施例中，bPL到PPL的转化以连续流形式在气相下执行。在某些实施例中，bPL到PPL的转化以连续流形式在液相下执行。在某些实施例中，bPL到PPL的转化以间歇或半间歇形式在液相下执行。bPL到PPL的转化可在多种条件下执行。在某些实施例中，可在促使bPL到PPL的转变的一或多种催化剂的存在下执行所述反应。

[0509] 在一些实施例中，进入聚合方法的产物流是气体或液体。聚合方法中的bPL到PPL的转化可以气相或液相来执行且可纯净的或在运载气体、溶剂或其它稀释剂的存在下执行。

[0510] 在某些变化形式中，聚合反应器的操作温度维持在聚丙内酯的裂解温度下或更低。在一些实施例中，反应区的温度维持在约150℃下或更低。在一些实施例中，聚合反应器的操作温度维持在约0℃到约200℃下。在一些实施例中，聚合反应器的操作温度维持在约25℃到约200℃下。在一些实施例中，聚合反应器的操作温度维持在约50℃到约150℃下。在一些实施例中，聚合反应器的操作温度维持在约70℃到约150℃下。在一些实施例中，聚合反应器的操作温度维持在约100℃到约150℃下。在一些实施例中，聚合反应器的操作温度维持在约0℃到约100℃下。在一些实施例中，聚合反应器的操作温度维持在约50℃到约100℃下。在一些变化形式中，操作温度是反应器的内容物的平均温度。

[0511] 在一些变化形式中，聚合反应器被配置成以从1秒到10小时、从1秒到3小时、从1分钟到2小时、从1.5分钟到90分钟、从2分钟到75分钟、从2分钟到60分钟、从2分钟到45分钟、从3分钟到30分钟或从4分钟到15分钟的驻留时间产生PPL。在一个实施例中，反应混合物的驻留时间从2分钟到90分钟。在某些变化形式中，驻留时间指一种材料在容器(例如反应容器)中所耗费的时间长度。所述时间长度可通过指定材料的体积流率和含有材料的容器的有效体积来计算。

[0512] 在一些变化形式中，聚合反应器被配置成在从0.01巴到100巴、从0.01巴到50巴、

从0.1巴到30巴、从1巴到20巴、从2巴到15巴、从3巴到10巴、从0.01巴到15巴、从0.01巴到10巴、从0.1巴到5巴或从0.1巴到2巴的操作压力下产生PPL。在一些实施例中，聚合反应器为CSTR且反应器中的操作压力从0.1巴到5巴。在其它实施例中，聚合反应器为PFR且反应器中的操作压力从1巴到约20巴。在其它实施例中，聚合反应器为环管反应器且反应器中的操作压力从1巴到约20巴。

[0513] 均相催化剂和引发剂

[0514] 任何合适的聚合引发剂和/或催化剂都可用于将进入PPL生产系统/生产方法的BPL产物流转化成PPL产物流。在一些实施例中，聚合引发剂或催化剂是均相的，且含有聚合反应混合物。能够将产物流转化为PPL产物流的任何合适的均相聚合引发剂或催化剂都可用于本文所描述的方法中。

[0515] 将适用于本文中所揭示方法的的开环聚合步骤的催化剂(例如)在以下揭示：美国化学学会杂志(Journal of the American Chemical Society)(2002)124(51)，15239到15248巨分子(Macromolecules)，第24卷、第20号，第5732到5733页，聚合物科学期刊(Journal of Polymer Science)，部分A-1，第9卷、第10号，第2775到2787页；Inoue，S.，Y.Tomoi、T.Tsuruta与J.Furukawa；巨分子，第26卷，第20号，第5533到5534页；巨分子，第23卷，第13号，第3206到3212页；聚合物预印本(Polymer Preprints)(1999)，40(1)，508到509；巨分子，第21卷，第9号，第2657到2668页；以及有机金属化学期刊(Journal of Organometallic Chemistry)，第341卷，第1到3号，第83-9页；以及在美国专利(USPatent)第3,678,069,3,169,945,6,133,402;5,648,452;6,316,590;6,538,101；以及6,608,170号中。所述专利中的每一个以全文引用的方式由此并入本文中。

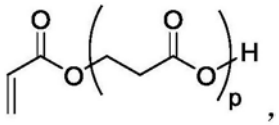
[0516] 聚合方法可另外包括聚合引发剂，所述聚合引发剂包含(但不限于)胺、多元胺、(尤其是)膦。此外，多种聚合引发剂可用于聚合方法中，所述聚合引发剂包含而不限于碱金属和碱土金属的碳酸盐。

[0517] 在某些实施例中，合适的聚合引发剂包含金属离子或有机阳离子的羧酸盐。

[0518] 在某些实施例中，聚合引发剂与含有bPL的产物流相组合。在某些实施例中，聚合引发剂与产物流中的bPL的摩尔比为约1:15000。在某些实施例中，聚合引发剂:bPL的摩尔比为约1:100、1:10000、1:1000、1:20000或包含任何两种这些比率的范围。

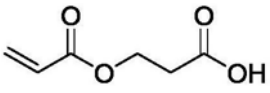
[0519] 在某些实施例(其中聚合引发剂包括羧酸盐)中，羧酸盐具有使得在bPL开始聚合时所产生的聚合物链具有丙烯酸酯链端的结构。在某些实施例中，在聚合引发剂上的羧酸盐离子为用于聚合方法中的链转移剂的阴离子形式。

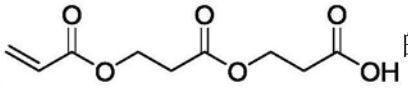
[0520] 在某些实施例中，聚合引发剂的羧酸盐为式(A)化合物的盐(即阴离子形式)：

[0521] ，

(A)

[0522] 或这些形式的任何两个或多于两个的混合物，其中p从0到9。在某些实施例中，p从0到5。在某些实施例中，聚合引发剂的羧酸盐为丙烯酸盐(即式(A)化合物，其中p＝0)。

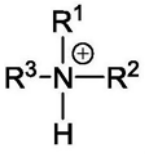
[0523] 在某些实施例中，聚合引发剂的羧酸盐为丙烯酸二聚体的盐。

在某些实施例中，聚合引发剂的羧酸盐为丙烯酸三聚体的盐。

[0524] 在某些实施例(其中聚合引发剂包括羧酸盐)中，羧酸盐为C_{1-40}羧酸的阴离子形式。在某些实施例中，羧酸盐可以是聚羧酸的盐(例如具有两个或多于两个羧酸基团的化合物)。在某些实施例中，羧酸盐包括C_{1-20}羧酸的阴离子。在某些实施例中，羧酸盐包括C_{1-12}羧酸的阴离子。在某些实施例中，羧酸盐包括C_{1-8}羧酸的阴离子。在某些实施例中，羧酸盐包括C_{1-4}羧酸的阴离子。在某些实施例中，羧酸盐包括任选地被取代的苯甲酸的阴离子。在某些实施例中，羧酸盐选自由以下组成的群组：甲酸盐、乙酸盐、丙酸盐、戊酸盐、丁酸盐、C_{5-10}脂族羧酸盐以及C_{10-20}脂族羧酸盐。

[0525] 如所提到，在某些实施例中，聚合引发剂包括有机阳离子的羧酸盐。在某些实施例中，聚合引发剂包括阳离子的羧酸盐，在所述阳离子中，正电荷至少部分地位于氮、硫或磷原子上。在某些实施例中，聚合引发剂包括氮阳离子的羧酸盐。在某些实施例中，聚合引发剂包括选自由以下组成的群组的阳离子的羧酸盐：铵、脒、胍、氮杂环的阳离子形式以及这些阳离子中的两个或多于两个的任何组合。在某些实施例中，聚合引发剂包括磷阳离子的羧酸盐。在某些实施例中，聚合引发剂包括选自由以下组成的群组的阳离子的羧酸盐：磷和磷腈。在某些实施例中，聚合引发剂包括含硫阳离子的羧酸盐。在某些实施例中，聚合引发剂包括锍盐。

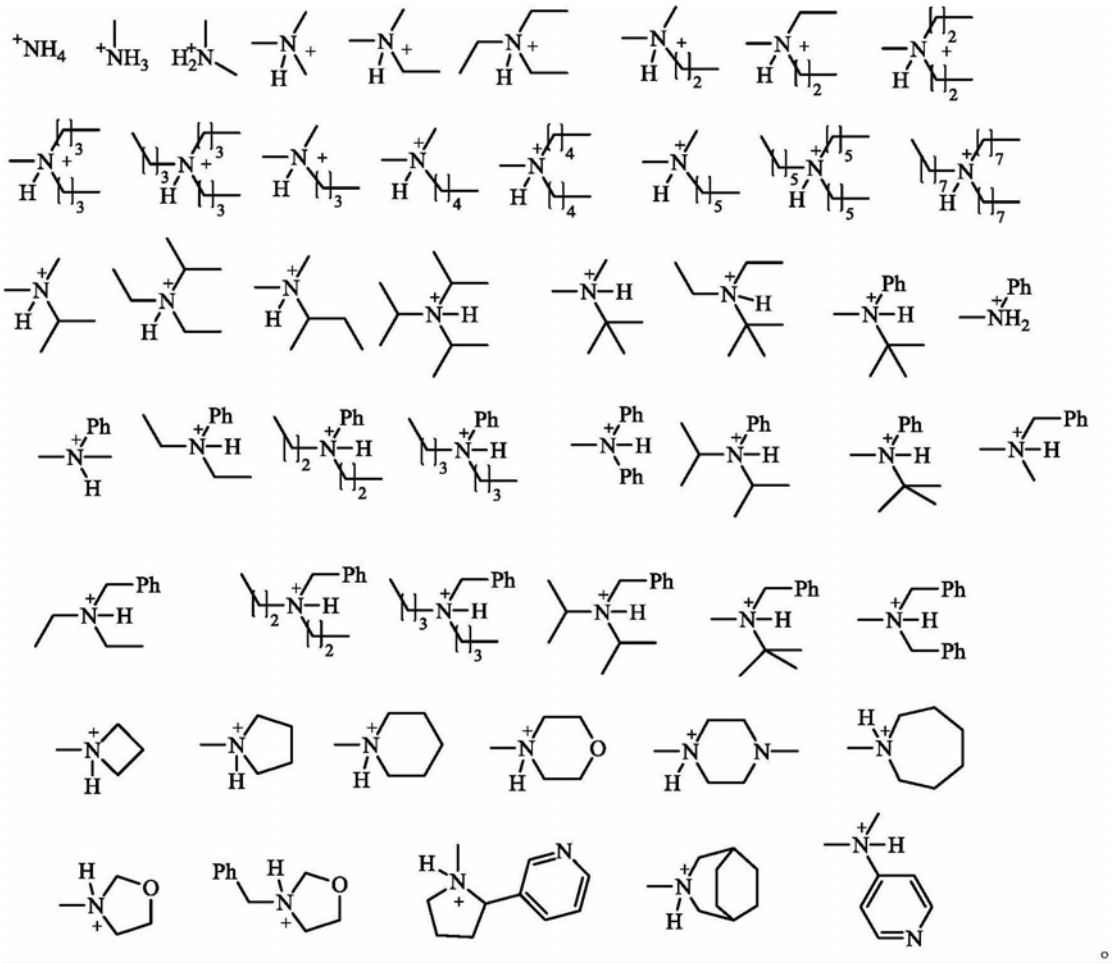
[0526] 在某些实施例中，聚合引发剂包括质子化胺的羧酸盐：

[0527] ，

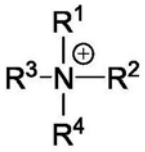
[0528] 其中：

[0529] 每一R^1和R^2独立地为氢或选自由以下组成的群组的任选地被取代的基团：C_{1-20}脂族；C_{1-20}杂脂族；3元到8元饱和或部分不饱和单环碳环；7到14元饱和或部分不饱和多环碳环；具有独立地选自氮、氧或硫的1到4个杂原子的5元到6元单环杂芳基环；具有独立地选自氮、氧或硫的1到5个杂原子的8元到14元多环杂芳基环；具有独立地选自氮、氧或硫的1到3个杂原子的3元到8元饱和或部分不饱和单环杂环；具有独立地选自氮、氧或硫的1到5个杂原子的6到14元饱和或部分不饱和多环杂环；苯基；或8元到14元多环芳香基环；其中R^1和R^2可利用中间原子结合在一起以形成任选地含有一或多个额外杂原子的一或多个任选地被取代的环；每一R^3独立地为氢或选自由以下组成的群组的任选地被取代的基团：C_{1-20}脂族；C_{1-20}杂脂肪族；3元到8元饱和或部分不饱和单环碳环；7元到14元饱和或部分不饱和多环碳环；具有独立地选自氮、氧或硫的1到4个杂原子的5元到6元单环杂芳基环；具有独立地选自氮、氧或硫的1到5个杂原子的8元到14元多环杂芳基环；具有独立地选自氮、氧或硫的1到3个杂原子的3元到8元饱和或部分不饱和单环杂环；具有独立地选自氮、氧或硫的1到5个杂原子的6到14元饱和或部分不饱和多环杂环；苯基；或8元到14元多环芳香基环；其中R^3基团可与R^1或R^2基团结合在一起以形成一或多个任选地被取代的环。

[0530] 在某些实施例(其中聚合引发剂包括质子化胺的羧酸盐)中，质子化胺选自由以下组成的群组：

[0531] 

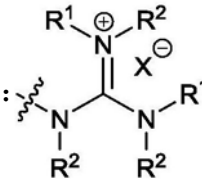
[0532] 在某些实施例中，聚合引发剂包括季铵盐的羧酸盐：

[0533] 

[0534] 其中：

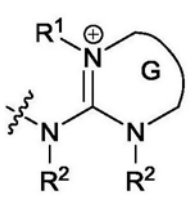
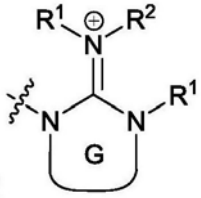
[0535] 每一R^1、R^2和R^3已在上文描述；且

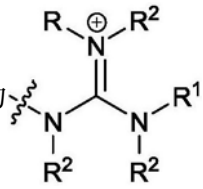
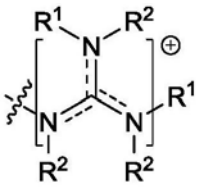
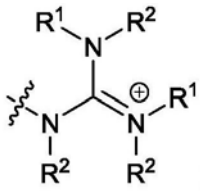
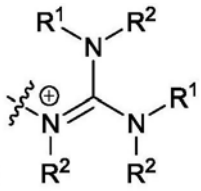
[0536] 每个R^4独立地为氢或选自由以下组成的群组的任选地被取代的基团：C_{1-20}脂族；C_{1-20}杂脂族；3元到8元饱和或部分不饱和单环碳环；7元到14元饱和或部分不饱和多环碳环；具有独立地选自氮、氧或硫的1到4个杂原子的5元到6元单环杂芳基环；具有独立地选自氮、氧或硫的1到5个杂原子的8元到14元多环杂芳基环；具有独立地选自氮、氧或硫的1到3个杂原子的3元到8元饱和或部分不饱和单环杂环；具有独立地选自氮、氧或硫的1到5个杂原子的6元到14元饱和或部分不饱和多环杂环；苯基；或8元到14元多环芳基环；其中R^4基团可与R^1、R^2或R^3基团结合在一起以形成一或多个任选地被取代的环。

[0537] 在某些实施例中，聚合引发剂包括胍基：的羧酸盐，其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述。在某些实施例中，每一R^1和R^2独立地

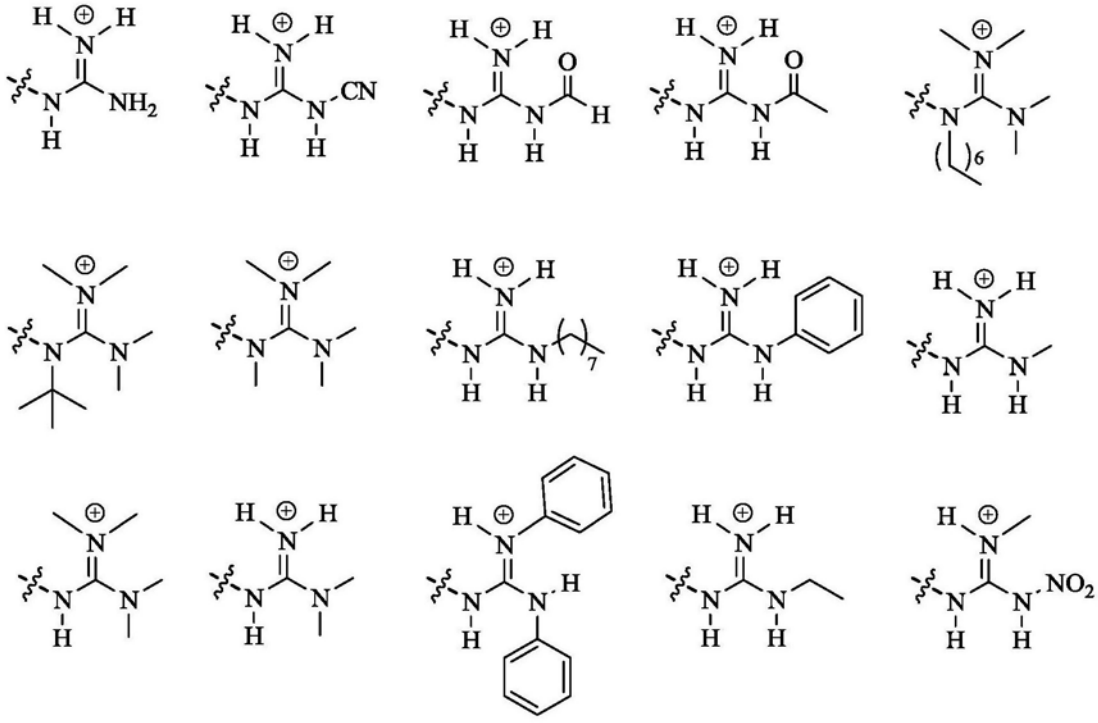
为氢或C_{1-20}脂族。在某些实施例中，每一R^1和R^2独立地为氢或C_{1-12}脂族。在某些实施例中，每一R^1和R^2独立地为氢或C_{1-20}杂脂族。在某些实施例中，每一R^1和R^2独立地为氢或苯基。在某些实施例中，每一R^1和R^2独立地为氢或8元到10元芳基。在某些实施例中，每一R^1和R^2独立地为氢或5元到10元杂芳基。在某些实施例中，每一R^1和R^2独立地为氢或3元到7元杂环。在某些实施例中，R^1和R^2中的一个或多个为任选地被取代的C_{1-12}脂族。

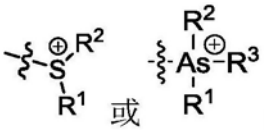
[0538] 在某些实施例中，任何两个或多于两个R^1或R^2基团利用中间原子结合在一起以形成一或多个任选地被取代的碳环、杂环、芳香基或杂芳基环。在某些实施例中，R^1和R^2基团结合在一起以形成任选地被取代的5元或6元环。在某些实施例中，三个或多于三个R^1和/或R^2基团结合在一起以形成任选地被取代的稠合环系统。

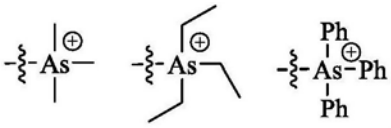
[0539] 在某些实施例中，R^1和R^2基团利用中间原子结合在一起以形成选自由以下的化合物： 或 ，其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述，且环G是任选地被取代的5元到7元饱和或部分不饱和杂环。

[0540] 应了解，当将胍阳离子描绘为时，全部这类共振形式由本揭示所预期且包含。举例来说，这类基团也可描绘为、或。

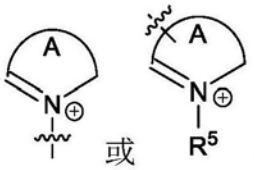
[0541] 在特定实施例中，胍阳离子选自由以下组成的群组：

[0542] 

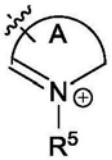
[0543] 在某些实施例中，聚合引发剂包括锍基团或砷基团的羧酸盐：，其中R^1、R^2和R^3中的每一个如上文所定义且在本文中的类别和子类中描述。

[0544] 在特定实施例中，砷阳离子选自由以下组成的群组：。

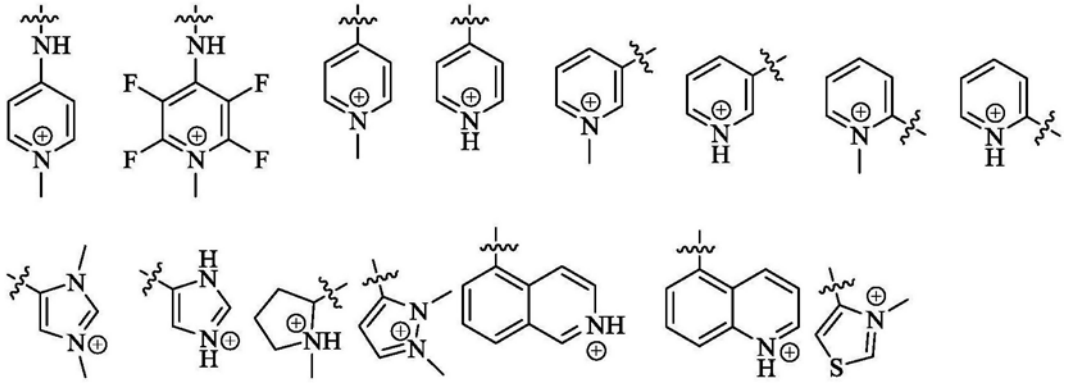
[0545] 在某些实施例中，聚合引发剂包括任选地被取代的含氮杂环的羧酸盐。在某些实施例中，含氮杂环为芳族杂环。在某些实施例中，任选地被取代的含氮杂环选自由以下组成的群组：吡啶、咪唑、吡咯啶、吡唑、喹啉、噻唑、二噻唑、恶唑、三唑、吡唑、异恶唑、异噻唑、四唑、吡嗪、噻嗪和三嗪。

[0546] 在某些实施例中，含氮杂环包含季铵化氮原子。在某些实施例中，含氮杂环包含亚铵部分，如在某些实施例中，任选地被取代的含氮杂环选自由以下组成的群组：吡啶、咪唑、吡咯烷、吡唑、喹啉、噻唑、二噻唑、恶唑、三唑、异恶唑、异噻唑、四唑、吡嗪、噻嗪和三嗪。

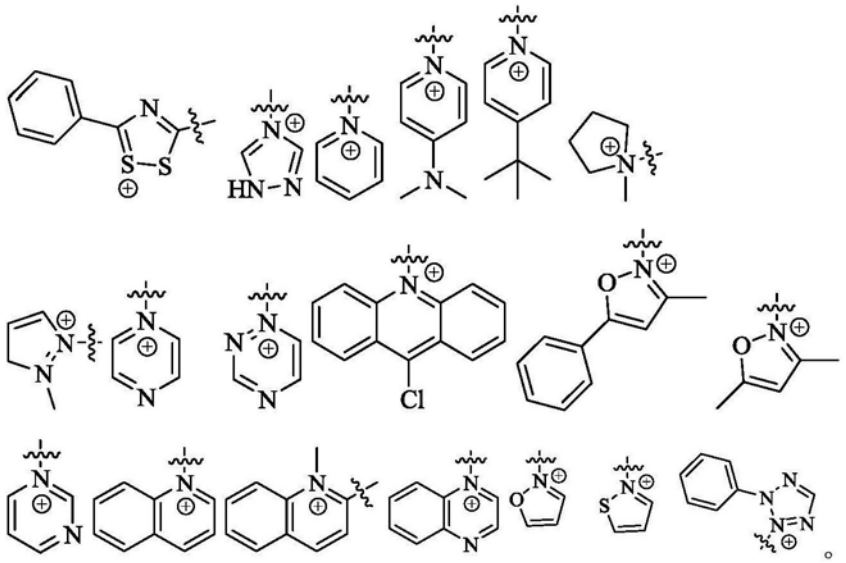
[0547] 在某些实施例中，含氮杂环经由环氮原子键连到金属错合物。在某些实施例中，进行附接的环氮进而被季铵化，且在某些实施例中，金属错合物的键连代替N-H键结且氮原子进而保持中性。在某些实施例中，任选地被取代的N连接的含氮杂环为吡啶衍生物。在某些实施例中，任选地被取代的N连接的含氮杂环为咪唑衍生物。在某些实施例中，任选地被取代的N连接的含氮杂环为噻唑衍生物。在某些实施例中，任选地被取代的N连接的含氮杂环为吡啶衍生物。

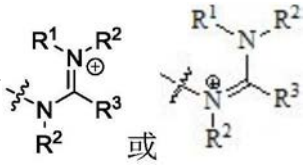
[0548] 在某些实施例中，聚合引发剂包括  的羧酸盐。在某些实施例中，环A为任选地被取代的5元到10元杂芳基。在某些实施例中，环A为任选地被取代的6元杂芳基。在某些实施例中，环A为稠合杂环的环。在某些实施例中，环A为任选地被取代的吡啶基。

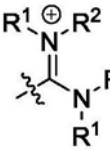
[0549] 在特定实施例中，含氮杂环阳离子选自由以下组成的群组：

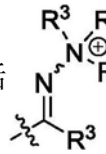


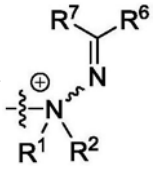
[0550]



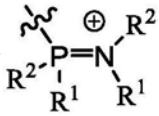
[0551] 在某些实施例中，聚合引发剂包括  的羧酸盐，其中每一R^1、R^2和R^3独立地如上文所定义且在本文中的类别和子类中描述。

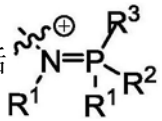
[0552] 在某些实施例中，聚合引发剂包括  的羧酸盐，其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述。

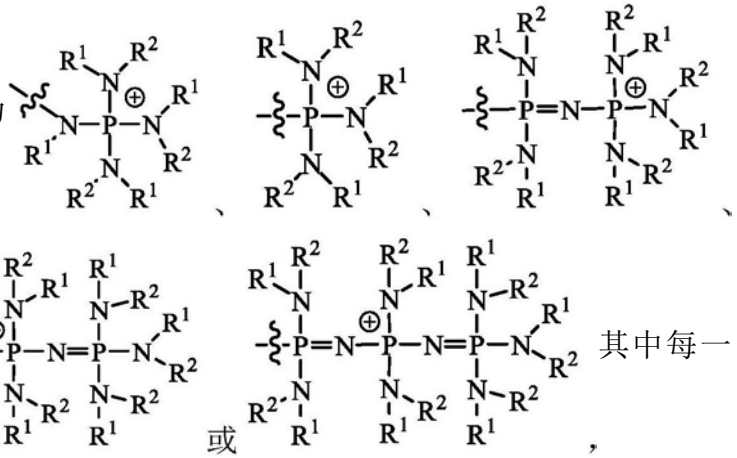
[0553] 在某些实施例中，聚合引发剂包括  的羧酸盐，其中每一R^1、R^2和R^3独立地如上文所定义且在本文中的类别和子类中描述。

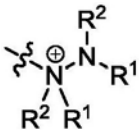
[0554] 在某些实施例中，聚合引发剂包括  的羧酸盐，其中R^1、R^2、R^6和R^7中的每一个独立地如上文所定义且在本文中的类别和子类中描述。

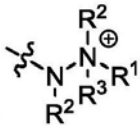
[0555] 在某些实施例中，R^6和R^7各独立地为选自由以下组成的群组的任选地被取代的基团：C_{1-20}脂族；C_{1-20}杂脂族；苯基，以及8元到10元芳基。在某些实施例中，R^6和R^7各独立地为任选地被取代的C_{1-20}脂族。在某些实施例中，R^6和R^7各独立地为任选地被取代的C_{1-20}杂脂族具有。在某些实施例中，R^6和R^7各独立地为任选被取代的苯基或8元到10元芳基。在某些实施例中，R^6和R^7各独立地为任选地被取代的5元到10元杂芳基。在某些实施例中，R^6和R^7可利用中间原子结合在一起以形成选自由以下组成的群组的一或多个环：任选地被取代的C_3-C_{14}碳环、任选地被取代的C_3-C_{14}杂环、任选地被取代的C_6-C_{10}芳基，以及任选地被取代的5元到10元杂芳基。在某些实施例中，R^6和R^7各独立地为任选地被取代的C_{1-6}脂族。在某些实施例中，R^6和R^7的在每次出现时独立地为甲基、乙基、丙基、丁基、戊基、己基、庚基、辛基或苯甲基。在某些实施例中，R^6和R^7在每次出现时独立地为全氟。在某些实施例中，R^6和R^7在每次出现时独立地为$-CF_2CF_3$。

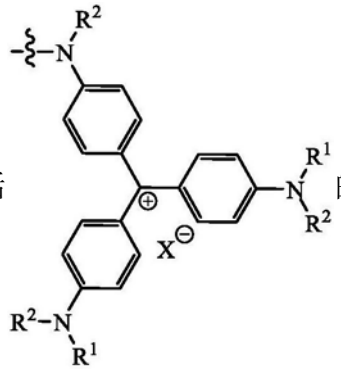
[0556] 在某些实施例中，聚合引发剂包括  的羧酸盐，其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述。

[0557] 在某些实施例中，聚合引发剂包括  的羧酸盐，其中每一R^1、R^2和R^3独立地如上文所定义且在本文中的类别和子类中描述。

[0558] 在某些实施例中，阳离子为  其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述。

[0559] 在某些实施例中，聚合引发剂包括的羧酸盐，其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述。

[0560] 在某些实施例中，聚合引发剂包括的羧酸盐，其中每一R^1、R^2和R^3独立地如上文所定义且在本文中的类别和子类中描述。

[0561] 在某些实施例中，聚合引发剂包括的羧酸盐，其中每一R^1和R^2独立地如上文所定义且在本文中的类别和子类中描述。在某些实施例中，合适的引发剂包含过渡金属化合物。在某些实施例中，合适的催化剂包含酸性催化剂。在某些实施例中，催化剂为非均相催化剂。

[0562] 在一些实施例中，均相聚合引发剂为季铵盐(例如丙烯酸四丁铵(TBA)、乙酸TBA、三甲基苯丙烯酸铵或三甲基苯乙酸铵)或磷化氢(例如四苯基丙烯酸磷)。

[0563] 在一些实施例中，催化剂为丙烯酸四丁铵、丙烯酸钠、丙烯酸钾、氯化铁、乙酸四丁铵、三甲基苯丙烯酸铵、三甲基苯乙酸铵或四苯基丙烯酸磷。

[0564] 参考图4A，在第一反应器(408)中的聚合催化剂和在第二反应器(410)中的额外聚合引发剂可相同或不同。举例来说，在一些实施例(其中相同引发剂用于两种反应器中)中，引发剂的浓度在每一反应器中并不相同。

[0565] 在一些实施例中，将均相聚合引发剂以液体形式添加到聚合反应器。在其它实施例中，以固体形式添加所述聚合引发剂，其随后在聚合反应中变为均相。在一些实施例(其中聚合引发剂以液体形式添加)中，可将聚合引发剂以熔融物或以任何合适的溶剂形式添加到聚合反应器。举例来说，在一些变化形式中，将GAA、熔融的PPL或bPL用作溶剂。

[0566] 在一些实施例中，选择用于聚合引发剂的溶剂以使得引发剂可溶，所述溶剂并不污染产物聚合物，且所述溶剂是无水的。在一些变化形式中，聚合引发剂溶剂为GAA、熔融PPL或bPL。在某些变化形式中，将固体PPL添加到聚合反应器，加热超过室温直到成液体，且用作聚合引发剂溶剂。在其它实施例中，将bPL添加到聚合反应器，冷却低于室温直到成液体，且用作聚合引发剂溶剂。

[0567] 在一些变化形式中，在一个位置中制备固体或液体聚合引发剂(在合适的溶剂中呈熔融或溶液形式)，随后运送到其在聚合反应器中使用的第二位置。在其它实施例中，在聚合反应器的位置处制备固体或液体聚合引发剂(在合适的溶剂中呈熔融或溶液形式)(例如以减少暴露于水分和/或氧气中)。

[0568] 可将固体或液体聚合引发剂(在合适的溶剂中呈熔融或溶液形式)泵抽到已搅拌的储料罐中或直接到聚合反应器中。

[0569] 在一些变化形式中,将液体引发剂和/或引发剂前体从运送容器(vessel/container)分配到中间、惰性容器中以与合适的溶剂相混合,且随后将引发剂溶液供应到反应器或预混合罐。可以此方式选择引发剂准备系统和连接件以确保引发剂或前体不由周围大气接触。

[0570] 在一些变化形式中,聚合反应器为PFR,将固体或液体引发剂(在合适的溶剂中呈熔融或溶液形式)以及bPL供应到小型搅拌罐,且随后将混合物供应到PFR。在其它实施例中,将bPL和液体催化剂供应到安装在PFR的入口处的预混合器。在又一实施例中,PFR具有静态混合器,所述反应发生在反应器的壳侧上,且将固体或液体引发剂以及bPL引入到反应器的入口处且静态混合器元件使引发剂与bPL相混合。在另外另一实施例中,PFR具有静态混合器,所述反应发生在反应器的壳侧上,且使用沿反应器的长度分布的多个位置处的计量泵/供应器将固体或液体引发剂引入到PFR中。

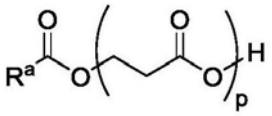
[0571] 在一些实施例中,将均相聚合引发剂以固体形式(例如固体Al(TPP)Et、固体丙烯酸钠、固体丙烯酸钾、固体醋酸钠、固体乙酸钾或固体TBA丙烯酸酯)递送到聚合反应器的位置,在惰性条件(CO或惰性气体)下将固体引发剂解封装并装载于料斗中,且可将所述固体从料斗直接供应到聚合反应器中或在反应器之前与bPL相混合或在泵送到聚合反应器或混合罐中之前计量加入合适的溶剂。

[0572] 非均相系统

[0573] 任何合适的聚合催化剂可用于聚合方法中以将进入聚合方法的产物流转化为PPL产物流。在一些实施例中,聚合催化剂为非均相且具有聚合反应混合物。能够使bPL在产物流中聚合以产生PPL产物流的任何合适的非均相聚合催化剂可用于本文所描述的方法中。

[0574] 在一些实施例中,非均相聚合催化剂包括上文所描述的负载于非均相载体上的均相聚合催化剂中的任一种。合适的非均相载体可包含(例如)无定形载体、层状载体或微孔载体,或其任何组合。合适的无定形载体可包含(例如)金属氧化物(如氧化铝或二氧化硅)或碳,或其任何组合。合适的层状载体可包含(例如)粘土。合适的微孔载体可包含(例如)沸石(如分子筛)或交联官能化聚合物。其它合适的载体可包含(例如)玻璃表面、硅石表面、塑料表面、包含沸石的金属表面、含有金属或化学涂覆的表面、膜片(包括例如耐纶、聚砜、硅石)、微珠(包括例如乳胶、聚苯乙烯或其它聚合物),以及多孔聚合物基质(包括例如聚丙烯酰胺、多醣、聚甲基丙烯酸酯)。

[0575] 在一些变化形式中,非均相聚合催化剂包括上文所描述的均相聚合催化剂中的任一种的羧酸盐,其中所述羧酸盐是非均相的。举例来说,在某些实施例中,聚合催化剂的羧酸盐为式(D)化合物:

[0576]  (D),

[0577] 其中p从0到9且R^a为非易失性部分。如本文中所使用,术语“非易失性部分”指羧酸盐可附接的部分或材料,且所述部分或材料致使羧酸盐(例如当p=0时)对于裂解条件为非易失性的。在一些实施例中,非易失性部分选自由以下组成的群组:玻璃表面、硅石表面、塑

料表面、包含沸石的金属表面、含有金属或化学涂覆的表面、膜片(包括例如耐纶、聚砜、硅石)、微珠(包括例如乳胶、聚苯乙烯或其它聚合物),以及多孔聚合物基质(包括例如聚丙烯酰胺、多醣、聚甲基丙烯酸酯)。在一些实施例中,非易失性部分具有超过100、200、500或1000g/mol的分子量。在一些实施例中,非易失性部分为固定或填充床系统的部分。在一些实施例中,非易失性部分为包括球粒(例如沸石)的固定或填充床系统的部分。在某些实施例中,p从0到5。在某些实施例中,聚合催化剂的羧酸盐为丙烯酸盐(即式(D)化合物的丙烯酸盐,其中p=0)。

[0578] 在一些实施例中,非均相聚合催化剂为固体载体型季铵盐(例如丙烯酸四丁铵(TBA)、乙酸TBA、三甲基苯丙烯酸铵或三甲基苯乙酸铵)或磷化氢(例如四苯基丙烯酸磷)。

[0579] 在一些实施例中,催化剂为固体载体型四丁基丙烯酸铵、氯化铁、乙酸TBA、四甲基苯丙烯酸铵、四甲基苯乙酸铵或四苯基丙烯酸磷。

[0580] 在某些实施例中,进入聚合方法的产物流到PPL产物流的转化利用固体羧酸盐催化剂进行且所述转化至少部分地在气相中进行。在某些实施例中,在聚合方法中的固体羧酸盐催化剂包括固体丙烯酸催化剂。在某些实施例中,产物流以液体形式进入聚合方法且与固体羧酸盐催化剂相接触以形成PPL产物流。在其它实施例中,产物流以气体形式进入聚合方法且与固体羧酸盐催化剂相接触以形成PPL产物流。

[0581] 在一些变化形式中,聚合催化剂为非均相催化剂床。任何合适的树脂可用于这种非均相催化剂床。在一个实施例中,聚合催化剂为填充在管状反应器中的非均相催化剂床。在一些实施例中,聚合反应器系统包括多个非均相催化剂床,其中至少一种催化剂床用于聚合反应器,且同时至少一种催化剂床并不用于聚合反应器。举例来说,未有效地使用的催化剂床可再生以用于稍后使用,或在有效使用的床催化失效的情况下,可存储为备用催化剂床。在一个实施例中,聚合反应器系统包括三种非均相催化剂床,其中一种催化剂床用于聚合反应器,一种催化剂床再生,且一种催化剂床在催化剂失效的情况下存储为备用。

[0582] 在一些变化形式中,非均相聚合催化剂在一个位置中制备,随后运送到其在聚合反应器中使用的第二位置。在其它实施例中,非均相聚合催化剂在聚合反应器的位置处制备(例如以减少暴露于水分和/或氧气中)。

[0583] 溶剂

[0584] 在一些实施例中,聚合方法不包含溶剂。在其它实施例中,聚合方法确实包含一或多种溶剂。合适的溶剂可包含(但不限于):烃、醚、酯、酮、腈、酰胺、砜、卤代烃以及类似物。在某些实施例中,选择溶剂以使得PPL产物流可溶于反应介质中。

[0585] 不希望受任何具体的理论所束缚,相信包括低到适中极性的路易斯(Lewis)碱的溶剂改良聚合反应的效能。因此,在某些实施例中,聚合溶剂包括路易斯碱且比1,3-二烷(ε=在20℃下的介电常数=13.6)极性更低。在某些实施例中,聚合溶剂包括路易斯碱且比邻二氟苯(ε=13)极性更低。在某些实施例中,聚合溶剂包括路易斯碱且比偏氟邻苯(ε=5)极性更低。在某些实施例中,聚合溶剂包括具有与1,4-二烷(ε=2.2)基本上相同极性的路易斯碱。在一些实施例中,在通过介电常数测量时,聚合溶剂比羰基化溶剂极性更低。在一些实施例中,聚合溶剂在20℃下具有低于约13.6、低于约13或低于约5的介电常数。

[0586] 举例来说,参考图4A和4B中所描绘的聚合方法,反应器408和/或410可被配置成接收溶剂。举例来说,在一种变化形式中,聚合方法可进一步包含被配置成将溶剂供应到反应

器408和410中的溶剂源。在另一变化形式中，来自产物流402的bPL可与溶剂相组合以形成含有被供应到反应器408中的bPL的产物流。在又另一变化形式中，来自聚合催化剂源404和/或406的聚合催化剂可与溶剂相组合以形成被供应到反应器中的聚合催化剂物流。

[0587] 聚合反应器

[0588] 在聚合方法中的一或多个聚合反应器可以是用于从进入聚合方法的产物流产生PPL产物流的任何合适的聚合反应器。举例来说，聚合反应器可以是CSTR、环管反应器或推流式反应器，或其一组合。在一些实施例中，聚合方法包括单个反应器，而在其它实施例中，聚合方法包括多个反应器。在一些变化形式中，bPL在聚合反应器中完全地转化为PPL。在其它变化形式中，bPL并未在聚合反应器中完全地转化为PPL，且从聚合反应器中排出的PPL物流包括未反应的bPL。在某些变化形式中，包括未反应bPL的PPL物流被引导到bPL/PPL分离器以将bPL从PPL中去除。可随后将bPL再循环回到聚合反应器中，如例如在上文的图7、9、11和13中所描述。

[0589] 在某些变化形式中，聚合方法包括两个串联的反应器，其中已纯化的bPL物流进入第一反应器且进行不完全聚合以产生包括PPL和未反应的bPL的第一聚合物流，所述第一聚合物流排出第一反应器的出口且进入第二反应器的入口以经历额外的聚合。在一些变化形式中，额外聚合使bPL完全地转化为PPL，且PPL产物流从第二聚合反应器的出口排出。

[0590] 在其它变化形式中，额外聚合使bPL不完全地转化为PPL，且PPL产物流从包括PPL和未反应的bPL的第二聚合反应器的出口排出。在某些变化形式中，PPL产物流进入BPL/PPL分离器以从PPL产物流中去除未反应的bPL。在某些变化形式中，将未反应的bPL再循环回到聚合方法中。举例来说，在一些变化形式中，将未反应的bPL再循环到第一聚合反应器或第二聚合反应器，或第一和第二聚合反应器两者。

[0591] 在一些实施例中，聚合方法包括后接BPL/PPL分离器(如在真空下操作的刮膜式蒸发器(WFE)或闪蒸罐蒸发器)的一系列一或多个连续CSTR反应器。在其它实施例中，聚合方法包括后接BPL/PPL分离器(如在真空下操作的WFE或闪蒸罐蒸发器)的一系列一或多个环管反应器。在又其它实施例中，聚合方法包括后接抛光推流式反应器(PFR)或BPL/PPL分离器(在真空下操作的刮膜式蒸发器或闪蒸罐蒸发器)的一系列一或多个CSTR反应器中的一系列一或多个。在又其它实施例中，聚合方法包括任选地后接BPL/PPL分离器(如在真空下操作的WFE或闪蒸罐蒸发器)的一系列一或多个PFR。

[0592] 在一些实施例中，聚合方法包括多余两个聚合反应器。举例来说，在某些实施例中，聚合方法包括三个或多于三个聚合反应器、四个或多于四个聚合反应器、五个或多于五个聚合反应器、六个或多于六个聚合反应器、七个或多于七个聚合反应器，或八个或多于八个聚合反应器。在一些变化形式中反应器串联布置，而在其它变化形式中，反应器并行布置。在某些变化形式中，反应器中的一些串联布置而其它反应器并行布置。

[0593] 图4A和4B描绘包括串联连接的两个聚合反应器的示范性PPL生产系统/生产方法，以及具有用于将未反应的bPL再循环回到聚合反应器中的刮膜式蒸发器(WFE)的PPL纯化和BPL再循环系统。参考图4A，聚合方法包含分别被配置成将bPL和催化剂供应到反应器408中的bPL源402和聚合催化剂源404。反应器408包含用以从bPL源接收bPL的bPL入口和用以从聚合催化剂源接收聚合催化剂的聚合催化剂入口。在一些变化形式中，bPL入口被配置成以3100kg/hr的速率从bPL源接收bPL，且第一聚合催化剂入口被配置成以0.1到5kg/hr的速率

从聚合催化剂源接收聚合催化剂。

[0594] 再次参考图4A，反应器408进一步包含用以将包括PPL、未反应的bPL以及残余羰基化催化剂的混合物输出到反应器410的混合物出口。反应器410为在反应器408之后定位的第二反应器，且被配置成从反应器408接收混合物且从聚合催化剂源406接收额外聚合催化剂。在一些变化形式中，第二反应器的混合物入口被配置成以4500kg/hr的速率从第一反应器接收混合物，且第二聚合催化剂入口被配置成以0.1到4kg/hr的速率从催化剂源接收额外聚合催化剂。

[0595] 再次参考图4A，反应器408进一步包含用以将包括PPL、未反应的bPL以及残余羰基化催化剂的混合物输出到蒸发器412的混合物出口。在一些变化形式中，混合物出口被配置成以4500kg/hr的速率输出这类混合物。

[0596] 参考图4B，所描绘的聚合方法包含分别被配置成将bPL和催化剂供应到反应器428中的bPL源422和聚合催化剂源424。反应器428包含用以从bPL源接收bPL的bPL入口和用以从聚合催化剂源接收聚合催化剂的聚合催化剂入口。在一些变化形式中，bPL入口被配置成以3100kg/hr的速率从bPL源接收bPL，第一催化剂入口被配置成以0.1到5kg/hr的速率从催化剂源接收催化剂。

[0597] 再次参考图4B，反应器428进一步包含用以将包括PPL、未反应的bPL以及残余羰基化催化剂的混合物输出到反应器430的混合物出口。反应器430为在反应器428之后定位的第二反应器，且被配置成从反应器428接收混合物且从聚合催化剂源426接收额外聚合催化剂。在一些变化形式中，第二反应器的混合物入口被配置成以4500kg/hr的速率从第一反应器接收混合物，且第二聚合催化剂入口被配置成以0.1到4kg/hr的速率从聚合催化剂源接收额外聚合催化剂。

[0598] 在一些变化形式中，从反应器410(图4A)和反应器430(图4B)输出的混合物由至少95％wt的PPL组成。

[0599] 这类混合物可从第二反应器输出到蒸发器。蒸发器412(图4A)和432(图4B)可以是例如刮膜式蒸发器、薄膜蒸发器或下降薄膜蒸发器。蒸发器被配置成产生PPL产物流。

[0600] 在一些变化形式中，蒸发器被配置成产生具有至少98％、至少98.5％或至少99％的纯度的PPL产物流。在其它变化形式中，蒸发器被配置成产生具有低于0.6％wt的bPL的PPL产物流。在一些变化形式中，PPL物流具有痕量的羰基化催化剂。举例来说，PPL产物流可具有来自羰基化催化剂的0.1mM的钴。在一些变化形式中，痕量的羰基化催化剂随后通过IER在热分解之前从PPL产物流中去除，如上文在图6、7、10和11中所描述。

[0601] 在一些变化形式中，聚合方法进一步包含一或多个热交换器。参考图4A，来自bPL源402的bPL可在这类BPL物流被供应到反应器408中之前穿过热交换器414。

[0602] 大体上应理解，所述聚合为放热反应。因此，在其它变化形式中，反应器408和410(图4A)可进一步包含到至少一个热交换器的连接件。参考图4B，反应器428和430(图4B)可进一步包含到至少一个热交换器的连接件。

[0603] 聚合方法的反应器可包含任何合适的反应器，所述反应器包含(例如)连续反应器或半分批反应器。在一种变化形式中，参考图4A，反应器可以是连续流动搅拌罐式反应器。反应器也可包含相同或不同的搅拌装置。举例来说，在一种变化形式中，反应器408可包含低速叶轮，如平板叶片。在其它变化形式中，反应器410可包含低剪应力混合器，如曲面叶

片。

[0604] 所属领域的技术人员将认识到，对于反应器中的每一个中的混合装置的选择可取决于各种因素，包含混合物在反应器中的粘度。举例来说，第一反应器中的混合物可具有小于1000cP的粘度。如果粘度小于1000cP，那么可能期望低速叶轮。在另一实例中，第二反应器中的混合物可具有大于2000cP的粘度。如果粘度大于2000cP，那么可能期望低剪应力混合器。

[0605] 在另一变化形式中，参考图4B，反应器可以是环管反应器。

[0606] 应理解，尽管图4A和4B描绘被配置成串联的两个反应器的使用，然而仍考虑其它配置。举例来说，在聚合方法的其它示范性变化形式中，可采用三个反应器。在其它变化形式(其中多个反应器用于聚合方法)中，其可串联或并行布置。

[0607] 图5描绘另一示范性聚合方法，其包含BPL聚合反应器。聚合反应器500包含被配置成使进入聚合方法的产物流与催化剂相混合的混合区域510，以及在混合区域之后定位的多个冷却区域520。聚合反应器500具有反应长度502，其中高达95％的在进入产物流中的bPL在催化剂的存在下聚合以在前25％的反应长度中形成PPL。在图5中所描绘的系统的一些变化形式中，bPL完全地转化为PPL。这种系统可用于(例如)bPL完全转化为如上文针对图6、8、10和12所描述的PPL中。

[0608] 在聚合反应器的一些变化形式中，多个冷却区域包含至少两个冷却区域。在一种变化形式中，多个冷却区包含两个冷却区域或三个冷却区域。

[0609] 举例来说，如图5中所描绘的聚合反应器500具有三个冷却区域522、524和526。在一种变化形式中，三个冷却区域串联连接在前25％的反应长度中。在另一变化形式中，冷却区域522被配置成以3100kg/hr的速率从混合区域接收bPL与催化剂的混合物；冷却区域524被配置成以3100kg/hr的速率接收bPL、催化剂与在冷却区域522中所产生的PPL的混合物；且冷却区域526被配置成以3100kg/hr的速率接收bPL、催化剂、在冷却区域522中所产生的PPL与在冷却区域524中所产生的PPL的混合物。

[0610] 在某些实施例中，前25％的反应长度为壳层和管式热交换器。在一种变化形式中，壳层可被配置成使热传递流体循环以在反应长度502中维持恒定温度。在另一变化形式中，管式热交换器被配置成去除在第一反应区域中所产生的热量。

[0611] 再次参考图5，聚合反应器500进一步包含连接到多个冷却区域520的结束转化区域528。在一些变化形式中，结束转化区域被配置成以3100kg/hr的速率接收bPL、催化剂与在多个冷却区域中所产生的PPL的混合物。在一种变化形式中，结束转化区不具有冷负荷。

[0612] 在一种变化形式中，聚合反应器为推流式反应器或管壳式反应器。

[0613] 用于本文中所描述方法的一或多个聚合反应器可由与聚合相容的任何合适的材料构成。举例来说，聚合反应器可由不锈钢或高镍合金或其一组合构成。

[0614] 在一些实施例中，聚合方法包括多个聚合反应器，且仅将聚合催化剂引入到在串联中的第一反应器中。在其它实施例中，将聚合催化剂单独地添加到在串联中的反应器中的每一个。举例来说，再次参考图4A，所描绘的是包括两个串联的CSTR聚合方法，其中将聚合催化剂引入到第一CSTR中，且将聚合催化剂单独地引入到第二CSTR中。在其它实施例中，使用单个推流式反应器(PFR)，且将聚合催化剂引入到反应器的起点处，而在其它实施例中，将聚合催化剂单独地引入到沿PFR的长度的多个位置处。在其它实施例中，使用多个

PFR,且将聚合催化剂引入到第一PRF的起点处。在其它实施例中,将聚合催化剂引入到所使用的每一PFR的起点处,而在其它实施例中,将聚合催化剂单独地引入到沿每一PFR的长度的多个位置处。

[0615] 聚合反应器可包括用以混合聚合反应混合物的任何合适的混合装置。合适的混合装置可包含(例如)轴向混合器、径向混合器、螺旋叶片、高剪应力混合器或静态混合器。合适的混合装置可包括单个或多个叶片,且可安装在顶部、底部或侧部。聚合反应器可包括单个混合装置或多个混合装置。在一些实施例中,使用多个聚合反应器,且每一聚合反应器包括相同类型的混合装置。在其它实施例中,每一聚合反应器包括不同类型的混合装置。在其它实施例中,一些聚合反应器包括相同混合装置,而其它聚合反应器包括不同混合装置。

[0616] 聚合子系统的优选实施例

[0617] 在优选实施例中,蒸馏子系统由(1)一或多个聚合反应器和(2)PPL纯化/BPL再循环系统组成。

[0618] 优选BPL聚合反应器

[0619] bPL的聚合可在串联或并行操作的一或多个反应器中执行,且在优选实施例中,将具有痕量的低沸点和高沸点杂质(非限制性杂质为THF和丁二酸酐)的基本上纯净的bPL(纯度大于99.9wt%)组成的馏出物流供应到bPL聚合反应器。bPL供应物流可在bPL纯化柱顶的温度(50到100℃)下供应或可在被供应到聚合反应器之前冷却到20到50℃。

[0620] 用于bPL的聚合的条件的优选组合包含在聚合引发剂的存在下、在低于或高于常压的压力下、在80到150℃,优选地120到145℃范围内的温度。优选引发剂为丙烯酸的季铵盐和碱金属盐。聚合引发剂的非限制性实例为丙烯酸钠、丙烯酸钾、四丁基丙烯酸铵。聚合引发剂与bPL的摩尔比为从1:20000到1:100,优选地从1:15000到1:500,优选地从1:10000到1:1000,且最优选地从1:8000到1:1500。

[0621] 在这类优选实施例中,在反应器之前将固体聚合引发剂与新鲜bPL物流相混合;高剪切混合器可用于实现bPL与引发剂的良好混合。在另一实施例中,在反应器之前使固体聚合引发剂与再循环bPL流相混合;高剪切混合器可用于实现bPL与引发剂的良好混合。在另一实施例中,聚合反应器如果直接供应到聚合反应器中;任选地,喷射器可用于使固体引发剂与供应到反应器的入口处的bPL中的全部或部分有效地混合。

[0622] 在用以形成PPL的bPL的聚合期间,充当链转移剂的丙烯酸可在原位形成。在一些实施例中,可将少量的丙烯酸供应到聚合反应器以控制PPL的分子量。为了避免丙烯酸的自由基聚合,可将如啡噻嗪(PTZ)的自由基聚合抑制剂供应到聚合反应器。自由基聚合抑制剂在反应器中的浓度维持在50到500ppm(按重量计);优选抑制剂浓度介于150到250ppm的范围内。

[0623] 如果将多个聚合反应器串联操作,那么可将bPL仅供应到第一反应器或bPL供应可在串联的反应器之间分路。如果将多个聚合反应器串联操作,那么可将聚合引发剂仅供应到第一反应器或可将引发剂供应到反串联的应器中的每一个。

[0624] 在优选实施例中的一个中,bPL的聚合可在串联操作的一或多个连续搅拌罐反应器(CSTR)中执行。聚合反应是放热的且反应的热量可通过本领域中已知的手段来去除,所述手段如内部热交换器或夹套、外部热交换器(反应混合物通过外部热交换器流通且已冷却的流返回到反应器)、蒸发冷却(反应器配备有附接的冷凝器:bPL从反应器中汽化、在冷

凝器中冷凝，且已冷却的bPL流返回到反应器)。反应器可在常压、低于常压、高于常压下操作。

[0625] 在另一优选实施例中，bPL的聚合可在串联操作的一或多个环管反应器中执行。反应器可在常压或高于常压下操作。与含有bPL与PPL的反应混合物相接触的表面的温度保持在防止PPL沉积(PPL熔点在约70到80℃)的温度下。

[0626] 在另一优选实施例中，bPL的聚合在由后接一或多个推流式反应器(PFR)的一或多个CSTR或环管反应器组成的反应器系统中执行。与含有bPL与PPL的反应混合物相接触的表面的温度保持在防止PPL沉积(PPL熔点在约70到80℃)的温度下。

[0627] 从反应系统(bPL转化)排出的流中的PPL的浓度大于40wt％，优选地大于60wt％，优选地大于75wt％。bPL的转化可大于80％、大于90％、大于95％或大于99％。从bPL聚合系统排出的流向前供应到PPL纯化和bPL再循环系统。在一个实施例中，聚合反应器产物流由约80wt％PPL、约20wt％bPL组成，且聚合引发剂并入到PPL分子中。

[0628] 优选PPL纯化/BPL再循环系统

[0629] 聚合反应器产物由PPL产物组成，且未反应的bPL向前供应到PPL纯化和bPL再循环系统。在优选实施例中，bPL可在于真空下操作的一或多个闪蒸蒸发器、或于真空下操作的一或多个刮膜式蒸发器(WFE)或其一组合中与PPL分离。为了避免bPL在这一系统内分解，与bPL相接触的表面温度保持在低于200℃，优选地低于180℃，最优选地低于160℃。将所回收的bPL供应回到聚合反应器。已纯化的PPL含有少于0.5wt％的bPL，优选地少于0.25wt％的bPL，优选地少于0.1wt％的bPL，且优选地bPL在PPL产物中的浓度低于100ppm。最优选地，将PPL向前供应到热分解反应系统以用于产生丙烯酸或粒化以用于存储或运送。

[0630] BPL转化

[0631] 在一些变化形式中，使介于5％与100％之间、介于10％与100％之间、介于20％与100％之间、介于30％与100％之间、介于40％与100％之间、介于50％与100％之间、介于60％与100％之间、介于70％与100％之间、介于80％与100％之间、介于90％与100％之间或介于95％与100％之间的bPL在聚合方法中转化为PPL。

[0632] 在一些变化形式中，bPL在聚合方法中部分地转化为PPL。举例来说，在一些变化形式中，bPL到PPL的完全转化大于或等于75％，且bPL到PPL的部分转化小于75％。在其它变化形式中，bPL到PPL的完全转化大于或等于80％，且bPL到PPL的部分转化小于80％。在其它变化形式中，bPL到PPL的完全转化大于或等于85％，且bPL到PPL的部分转化小于85％。在其它变化形式中，bPL到PPL的完全转化大于或等于90％，且bPL到PPL的部分转化小于90％。在其它变化形式中，bPL到PPL的完全转化大于或等于95％，且bPL到PPL的部分转化小于95％。在一种变化形式中，bPL到PPL的完全转化大于或等于99％，且bPL到PPL的部分转化小于99％。

[0633] 在其它变化形式中，部分转化介于30％与90％之间；介于40％与90％之间、介于50％与90％之间；或介于60％与90％之间。

[0634] 在一些变化形式中，聚合方法包括多个聚合反应器，且在每一反应器中bPL到PPL的转化介于5％与100％之间、介于10％与100％之间、介于20％与100％之间、介于30％与100％之间、介于40％与100％之间、介于50％与100％之间、介于60％与100％之间、介于70％与100％之间、介于80％与100％之间、介于90％与100％之间，或介于95％与100％之间的bPL转化为PPL。

[0635] 在一些变化形式中，聚合方法包括多个聚合反应器，且跨越整个聚合方法中bPL到PPL的转化介于5％与100％之间、介于10％与100％之间、介于20％与100％之间、介于30％与100％之间、介于40％与100％之间、介于50％与100％之间、介于60％与100％之间、介于70％与100％之间、介于80％与100％之间、介于90％与100％之间，或介于95％与100％之间的bPL转化为PPL。

[0636] 在一种变化形式中，两个反应器串联操作，且在每一反应器中bPL到PPL的转化介于10％与100％之间。

[0637] 如上文在图9到13中所描述，在如本文中所描述的用以产生PPL的方法的一些实施例中，bPL完全地转化为PPL。在其它实施例中，bPL部分地转化为PPL。

[0638] BPL转化

[0639] 不希望受任何理论所束缚，当反应物的浓度高且产物的浓度低时，bPL到PPL的聚合快速地进行。随着反应发展以产生更多产物，转化的驱动力降低。这一现象导致执行全部转化的反应器大于执行部分转化的那些反应器。因此，在某些实施例中，选择聚合条件和反应器大小以使得bPL到PPL的转化是部分的(例如70％转化)，且bPL/PPL分离装置(例如WFE或蒸馏柱)用于将反应物再循环回到反应器的入口。不希望受任何理论所束缚，这可避免对相对较大的反应器的需求而同时仍产生相对纯净的产物。另外，去除未反应的bPL，这可使对PPL的操控更容易。在无PPL分离的情况下，bPL的去除降低其它产物在热分解反应期间形成的可能性。

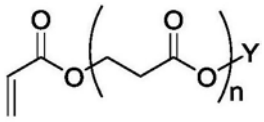
[0640] PPL产物流

[0641] 在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr PPL、至少约2500kg/hr PPL、至少约3000kg/hr PPL、至少约3050kg/hr PPL，或至少约3500kg/hr PPL、至少约3638kg/hr PPL、至少约4000kg/hr PPL、至少约5000kg/hr PPL、至少约1000kg/hr PPL、至少约20000kg/hr PPL或至少约35000kg/hr PPL。在一些实施例中，生产系统/生产方法可产生约2000kg/hr PPL、约2500kg/hr PPL、约3000kg/hr PPL、约3500kg/hr PPL、约3638kg/hr PPL、约4000kg/hr PPL、约5000kg/hr PPL、约1000kg/hr PPL、约20000kg/hr PPL或约35000kg/hr PPL。在一些实施例中，生产系统/生产方法可产生介于2000kg/hr与3500kg/hr之间的PPL、介于2500kg/hr与3500kg/hr之间的PPL、介于3000kg/hr与3500kg/hr之间的PPL、介于2000kg/hr与35000kg/hr之间的PPL、介于2500kg/hr与35000kg/hr之间的PPL、介于3000kg/hr与35000kg/hr之间的PPL、介于3500kg/hr与35000kg/hr之间的PPL、介于3638kg/hr与35000kg/hr之间的PPL、介于4000kg/hr与35000kg/hr之间的PPL、介于5000kg/hr与35000kg/hr之间的PPL、介于1000kg/hr与35000kg/hr之间的PPL，或介于20000kg/hr与35000kg/hr之间的PPL。

[0642] 在一些实施例中，生产系统/生产方法可产生至少约25kmol/hr PPL、至少约30kmol/hr PPL、至少约40kmol/hr PPL、至少约42kmol/hr PPL或至少约50kmol/hr PPL。在一些实施例中，在聚合之后，PPL在生产系统/生产方法中的PPL产物流中的质量分数可为至少约0.90、至少约0.95、至少约0.98、至少约0.982以及至少约0.99。在一些实施例中，在聚合之后，PPL在生产系统/生产方法中的PPL产物流中的摩尔分数可为至少约0.90、至少约0.95、至少约0.98、至少约0.984以及至少约0.99。PPL产物流的其余部分可包含未反应的bPL(以最多约0.02、最多约0.015或最多约0.011的摩尔分数)、如丁二酸酐(以最多约0.01、

最多约0.005或最多约0.004的摩尔分数)的副反应产物,以及剩余溶剂(例如THF)和剩余羰基化催化剂或其组分(以最多约1000ppm)。PPL产物流可随后接收热分解处理以形成GAA。在一些实施例中,生产系统/生产方法的PPL产物流可具有介于约50到150℃之间、介于约110到150℃之间或约145℃的温度。在一些实施例中,生产系统/生产方法的PPL产物流可处在至少约0.001巴、约0.001到1巴或至少约0.005巴的压力下。

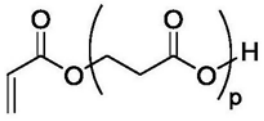
[0643] 在某些实施例中,提供一种用于产生(例如整合产生)包括式(B)的PPL链的组成物的方法:

[0644] 

(B)

[0645] 其中n为从10到约1,000的整数,且Y为-H或阳离子,

[0646] 所述方法包括在选自由以下组成的群组的链转移剂的存在下使bPL聚合的步骤:式(C)化合物:

[0647] ,

(C)

[0648] 或其盐,或这些化合物中的任何两个或多于两个的混合物,其中p从0到9。在某些实施例中,组成物进一步包括PPL。

[0649] 在某些实施例中,所形成的PPL组成物特征在于:所述组成物中的至少90%、95%、99%、99.5%、99.8或99.9%的聚合物链具有丙烯酸酯端基。

[0650] 在某些实施例中,所形成的PPL组成物特征在于:所述组成物中的至少90%、95%、99%、99.5%、99.8或99.9%的聚合物链具有式(B)。

[0651] 在某些实施例中,n(平均在聚丙内酯组成物中)介于10与50之间,或介于50与100之间,或介于100与150之间,或介于150与250之间,或介于250与350之间,或介于350与500之间。

[0652] 在一些实施例中,本文中所描述的系统被配置成产生具有以下平均分子量的聚丙内酯:介于800g/mol与100000g/mol之间、介于500g/mol与70000g/mol之间、介于1000g/mol与60000g/mol之间或介于1500g/mol与40000g/mol之间。在一些实施例中,分子量为数目平均分子量,而在其它实施例中,分子量为重均分子量。

[0653] 在某些实施例中,PPL组成物特征在于其具有小于10的多分散指数(PDI)。

[0654] 在某些实施例中,PPL组成物特征在于其具有小于8、或小于5、或小于3、或小于2.5或小于2.0的PDI。

[0655] 从PPL中去除钴/离子

[0656] 在一些实施例中,处理PPL产物流以降低钴和/或离子的浓度。钴可以是钴离子或不带电荷的的钴,或其一组合。所述离子可以是钴离子或非钴离子。

[0657] 在某些变化形式中,钴为钴离子。钴可来自羰基化催化剂、包括钴的残余催化剂组分,或残余催化剂或其组合的分解。举例来说,在一些实施例中,羰基化催化剂分解以产生

Co^{-1}、Co、Co^{+}、Co^{2+}或Co^{3+}，或其组合。因此，在一些实施例中，钴为钴离子，而在其它实施例中，钴并不是钴离子。

[0658] 在一些变化形式中至少一些离子从PPL产物流中去除。在一些变化形式中，离子包括金属离子。在其它实施例中，离子包括非金属离子。在其它实施例中，离子包括金属离子和非金属离子两者。如上文所论述，在某些变化形式中，离子包括钴离子。所述离子可来自羰基化催化剂、包括离子的残余催化剂组分、残余催化剂，或作为羰基化反应的副产品而产生的离子，或其组合的分解。举例来说，在一些实施例中，羰基化催化剂分解以产生Co^{-1}、Co、Co^{+}、Co^{2+}、Co^{3+}或Al^{3+}，或其组合。在其它实施例中，作为羰基化反应的副产品而产生的离子包含乙酸酯($CH_3C(O)O^-$)或丙烯酸酯($CH_2=CHC(O)O^-$)，或其一组合。

[0659] 在某些实施例中，处理PPL产物流以去除钴和/或离子的至少部分的步骤包括使用离子交换材料来进行钴和/或离子的离子交换。在一些实施例中，有可能使用用于离子交换材料的离子交换树脂。离子交换材料可以是阳离子、阴离子、两性的、路易斯碱、路易斯酸或可包括螯合剂群组。在某些实施例中，离子交换材料可以是阳离子交换剂。在某些实施例中，在阳离子交换材料上的官能团可选自：$-SO_3$、$PO3^{2-}$、-COOH、$-C_6H_4OH$、-SH、$-AsO_3$或$-SeO_3$或这些官能团中的两个或多于两个的组合。在某些实施例中，在阳离子交换材料上的官能团包括$-SO_3$。

[0660] 在某些实施例中，离子交换材料可以是阴离子交换剂。在某些实施例中，在阴离子交换材料上的官能团可选自：$-N^+$(烷基)$_3$、$-N^+(CH_3)_3$、$-N^+(CH_3)_2C_2H_4OH$、$-N^+(CH_3)_2C_2H_5$、$-P^+$(烷基)$_3$、$-P^+$(芳基)$_3$、$-P^+(C_4H_9)_3$，或$-P^+(Ph)_3$或这些官能团中的两个或多于两个的组合。在某些实施例中，在阴离子交换材料上的官能团包括$-N^+$(烷基)$_3$。在某些实施例中，在阴离子交换材料上的官能团包括$-P^+$(烷基)$_3$。在某些实施例中，在阴离子交换材料上的官能团包括$-P^+$(芳基)$_3$。

[0661] 在某些实施例(其中处理PPL产物流以分离钴和/或离子的步骤包括离子交换)中，所述过程需要阴离子交换和阳离子交换两者。在某些实施例中，阴离子和阳离子交换同时执行。在某些实施例中，阴离子和阳离子交换相继地执行。在某些实施例中，首先执行阴离子交换，随后是阳离子交换。在某些实施例中，首先执行阳离子交换，随后是阴离子交换。在某些实施例中，有机离子交换树脂被证实在包括有机离子交换树脂的分离步骤中可能是有用的。这类树脂的大体特征和特性与先前所描述的相同。

[0662] 在各种方面中，珠的大小可广泛分布，或可极窄，所谓单分散树脂。在实施例(其中催化剂通过离子交换从PPL产物流中移除)中，离子交换材料可通过任何常规方法与PPL产物流相接触。这种接触包含但不限于：使PPL产物流流动通过固体离子交换材料(即呈珠、颗粒或其它粒子形式)的固定床；使PPL产物流流动通过吸附剂的流化床，使PPL产物流流动通过包括离子交换材料的织物、网状物或过滤板，或使PPL产物流与离子交换材料浆化(通常后接过滤、离心、沉淀或类似步骤以从PPL产物流中去除离子交换材料)。在实施例(其中PPL产物流流动通过离子交换材料的填充柱)中，可能需要提供与供应件并行的多个这类柱以将流体从一个柱周期性地切换到另一个。因此，当离子交换材料的一个柱在钴和/或离子从PPL产物流中移除的情况下变得饱和时，其可切换到流动路径之外且流体转移到新鲜柱——在某些实施例中，从柱被放置在流动路径中到其被切换到流动路径之外的时间的间隔对应于本文中所描述的方法中所述的“第一时间间隔”。

[0663] 在离子交换材料用于从PPL产物流中去除钴和/或离子时，本发明方法可包含从离子交换材料中去除钴和/或离子的后续步骤。这类去除方法在本领域中所熟知且通常涉及使离子交换树脂与盐的浓溶液，所述盐的阴离子或阳离子将使吸附的组分从离子交换材料中转移。

[0664] 在某些变化形式中，钴是Co^{-1}、Co、Co^{+}、Co^{2+}或Co^{3+}，或其一组合。在一些实施例中，PPL产物流在钴去除之前具有介于0.001mM与5mM之间、介于0.01mM与3mM之间、介于0.01mM与2mM之间、介于0.01mM与1mM之间、介于0.05mM与0.5mM之间、介于0.05mM与0.2mM之间或介于0.07mM与0.15mM之间的钴浓度。在一些实施例中，在钴去除之前，渗透液的钴浓度为约0.01mM、约0.03mM、约0.06mM、约0.09mM、约0.1mM、约0.13mM、约0.16mM、约0.19mM、约0.2mM、约0.23mM、约0.26mM、约0.29mM或约0.3mM。在一个实施例中，在钴去除之前，PPL的钴浓度为约0.1mM。

[0665] 因此，在一些实施例中，在接触离子交换树脂之前，PPL产物流中钴的浓度介于0.001mM与5mM之间、介于0.01mM与3mM之间、介于0.01mM与2mM之间、介于0.01mM与1mM之间、介于0.05mM与0.5mM之间、介于0.05mM与0.2mM或介于0.07mM与0.15mM之间之间。

[0666] 在一些实施例中，在接触离子交换树脂之后，PPL产物流中钴的浓度介于0.001mM与1mM、0.001mM与0.5mM之间、介于0.001mM与0.05mM之间、介于0.005mM与0.02mM之间或介于0.007mM与0.015mM之间。在一种变化形式中，在接触离子交换树脂之后，PPL产物流中钴的浓度为0.01mM。

[0667] 在一些实施例中，至少一些铝从PPL产物流中去除。在某些变化形式中，铝为Al^{3+}。在一些实施例中，在铝去除之前，PPL产物流具有介于0.001mM与5mM之间、介于0.01mM与3mM之间、介于0.01mM与2mM之间、介于0.01mM与1mM之间、介于0.05mM与0.5mM之间或介于0.09mM与0.2mM之间的铝浓度。在一些实施例中，在铝去除之前，PPL产物流具有约0.01mM、约0.03mM、约0.06mM、约0.09mM、约0.1mM、约0.13mM、约0.16mM、约0.19mM、约0.2mM、约0.23mM、约0.26mM、约0.29mM或约0.3mM的铝浓度。在一个实施例中，在铝去除之前，PPL产物流的铝浓度为约0.1mM。

[0668] 因此，在一些实施例中，在接触离子交换树脂之前，PPL产物流中铝的浓度介于0.001mM与5mM之间、介于0.01mM与3mM之间、介于0.01mM与2mm之间、介于0.01mM与1mm之间、介于0.05mM与0.5mM之间、介于0.05mM与0.2mM之间或介于0.07mM与0.15mM之间。

[0669] 在一些实施例中，在接触离子交换树脂之后，PPL产物流中铝的浓度介于0.001mM与1mM、0.001mM与0.5mM之间、介于0.001mM与0.05mM之间、介于0.005mM与0.02mM之间或介于0.007mM与0.015mM之间。在一种变化形式中，在接触离子交换树脂之后，PPL产物流中铝的浓度为0.01mM。

[0670] 固体PPL

[0671] 在一些实施例中，本文中所描述的生产系统/生产方法进一步包括被配置成接收PPL产物流并产生固体PPL的PPL物流处理系统。举例来说，在一个实施例中，将PPL产物流供应到PPL流处理系统的至少一个入口中，且固体PPL从PPL流处理系统的至少一个出口排出。PPL流处理系统可被配置成以任何合适的形式产生固体PPL。举例来说，在一些实施例中，PPL流处理系统被配置成以球粒形式、成片形式、颗粒形式或挤压形式或其任何组合产生固体PPL。因此，固体PPL薄片、固体PPL球粒、固体PPL颗粒或固体PPL挤出物或其任何组合可从

PPL流处理系统的出口排出。PPL流处理系统可包含一或多个剥落装置、粒化装置、挤塑装置或粒化装置或其任何组合。

[0672] 地理位置

[0673] 在某些实施例中，本文中所描述的生产系统/生产方法在第一位置处产生PPL产物流，处理PPL产物流以产生固体PPL，且在第二位置中将固体PPL转化为GAA产物流。在一些实施例中，第一位置与第二位置至少相隔100英里。在某些实施例中，第一位置与第二位置相隔介于100与12,000英里之间。在某些实施例中，第一位置与第二位置相隔至少250英里、至少500英里、至少1,000英里、至少2,000或至少3,000英里。在某些实施例中，第一位置与第二位置相隔介于约250与约1,000英里之间、相隔介于约500与约2,000英里之间、相隔介于约2,000与约5,000英里之间或相隔介于约5,000与约10,000英里之间。在某些实施例中，第一位置和第二位置在不同国家中。在某些实施例中，第一位置和第二位置在不同大陆上。

[0674] 在某些实施例中，固体PPL从第一位置运送到第二位置。在一些实施例中，固体PPL运送超过100英里、超过500英里、超过1,000英里、超过2,000英里或超过5,000英里的距离。在某些实施例中，固体PPL运送介于100与12,000英里之间、介于约250与约1000英里之间、介于约500与约2,000英里之间、介于约2,000与约5,000英里之间或介于约5,000与约10,000英里之间的距离。在一些实施例中，固体PPL从第一国家运送到第二国家。在某些实施例中，固体PPL从第一大陆运送到第二大陆。

[0675] 在某些实施例中，固体PPL从北美洲运送到欧洲。在某些实施例中，固体PPL从北美洲运送到亚洲。在某些实施例中，固体PPL从US运送到欧洲。在某些实施例中，固体PPL从US运送到亚洲。在某些实施例中，固体PPL从中东运送到亚洲。在某些实施例中，固体PPL从中东运送到欧洲。固体PPL可通过任何合适的手段来运送，包含(例如)通过卡车、列车、油轮、驳船或轮船或这些手段的任何组合。在一些实施例中，固体PPL通过选自卡车、列车、油轮、驳船以及轮船中的至少两种方法来运送。在其它实施例中，固体PPL通过选自卡车、列车、油轮、驳船以及轮船中的至少三种方法来运送。

[0676] 在一些实施例中，固体PPL呈球粒、薄片、颗粒或挤出物，或其任何组合的形式。在一些变化形式中，使用如本文中所描述的热分解反应器将固体PPL转化为GAA产物流。在一些变化形式中，固体PPL被供应到中热分解反应器的入口且转化为GAA产物流。在其它实施例中，固体PPL转化为熔融PPL，且熔融PPL被供应到如本文中所描述的热分解反应器的入口中且转化为GAA产物流。

[0677] 丙烯酸生产系统/生产方法

[0678] 聚丙内酯(PPL)可根据以下方案大体上转化为丙烯酸(AA)：

[0679] 

PPL AA

[0680] 在某些实施例中，所产生的聚丙内酯不断地进行热分解(例如在供应分批反应器或其它连续流式反应器形式中)。在某些实施例中，使连续热分解过程链接到连续聚合方法从而以与反应器的消耗速率相匹配的速率提供丙烯酸。

[0681] 热分解反应器

[0682] 在一些实施例中，热分解反应器为流化床反应器。惰性气体可用于使惰性固体传热介质(HTM)流化，且将聚丙内酯供应到反应器。在一些变化形式中，可例如经由喷射嘴将聚丙内酯以熔融形式供应到反应器。熔融形式可有助于促进聚丙内酯在反应器内部的分散。

[0683] 反应器可配备有使HTM固体返回到反应器的旋流器。将惰性气体、冰丙烯酸以及更高沸点的杂质(如丁二酸酐和丙烯酸二聚体)从旋流器供应到杂质分离的部分冷凝器。举例来说，冷凝器可用于使高沸点杂质冷凝，且这类杂质可随后从反应器中吹扫为残余废物流。

[0684] 可将具有惰性气体的冰丙烯酸供应到使冰丙烯酸与惰性气体分离的第二冷凝器。液体冰丙烯酸流从第二冷凝器输出，且惰性气体输出为可返回到反应器以流化热传递固体的分离流。冰丙烯酸流可用于冷凝/吸收且随后存储。

[0685] 从反应器中吹扫的残余废物流可包含(例如)高沸点有机物(或有机重物质)(例如由聚合催化剂和丁二酸酐所产生)，以及阳离子和阴离子羰基化催化剂物种(如果羰基化催化剂不在热分解反应器之前分离)。在一些实施例中，高沸点有机物(或有机重物质)可包含非丙烯酸的任何化合物。在某些实施例中，高沸点有机物(或有机重物质)可包含在丙烯酸在冰丙烯酸生产系统/生产方法中冷凝之后保留在底部物流中的任何化合物。在一些实施例中，高沸点有机物(或有机重物质)可包含丁二酸酐、聚合催化剂或羰基化催化剂或其组分(例如来自羰基化催化剂的有机化合物)。在一些实施例中，高沸点有机物(或有机重物质)具有高于丙烯酸的沸点。

[0686] 在其它实施例中，热分解反应器为动态床反应器。将聚丙内酯以固体形式供应到动态床反应器中且冰丙烯酸以蒸气流形式从反应器中排出且随后冷凝。

[0687] 条件

[0688] 在一些变化形式中，热分解反应器中的操作温度从约150℃到约300℃、从约150℃到约200℃、从约150℃到约250℃、从约175℃到约300℃、从约200℃到约250℃、从约225℃到约275℃、从约250℃到约300℃、从约200℃到约300℃、从约200℃到约400℃或从约200℃到约500℃。在一些变化形式中，操作温度为反应器的内容物的平均温度。

[0689] 在一些变化形式中，热分解反应器中的操作压力从约0.01大气压到约500大气压(绝对)、从约0.01大气压到约10大气压(绝对)、从约0.01大气压到约50大气压(绝对)、从约1大气到约10大气压(绝对)、从约1大气到约50大气压(绝对)、从约1大气到约100大气压(绝对)、从约10大气压到约50大气压(绝对)、从约10大气压到约100大气压(绝对)、从约50大气压到约100大气压(绝对)、从约50大气压到约200大气压(绝对)、从约100大气压到约200大气压(绝对)、从约100大气压到约250大气压(绝对)、从约200大气压到约300大气压(绝对)、从约200大气压到约500大气压(绝对)或从约250大气压到约500大气压(绝对)。

[0690] 在尤其优选的实施例中，来自bPL聚合系统的PPL流以固相或液相、在介于100℃与320℃之间的温度下以及在介于1mmHg与5000mmHg之间的绝对压力下进入初级热分解反应器。许多方法中的一个可提供热传递输入(例如内部线圈)、具有来自和回到初级反应器的回路的外部热交换器或在反应器的壁上的阻挡夹套。替代地，可引入并不显著影响反应化学的高温液体或气体以维持期望的反应温度且在下游分离。取决于时间和温度，完全转化的驻留时间可在几秒到24小时或更长的范围内变化。反应器的内容物的混合也可改良质量和热传递。

[0691] 优选地，热分解条件和布置将使PPL到聚丙烯酸的损耗最小化。避免聚丙烯酸产物的代表性方式包含使用解聚催化剂以降低所要求的反应强度以降低丙烯酸到聚丙烯酸的反应速率(相对于PPL到丙烯酸)；使用高含量的自由基聚合抑制剂；和/或用以使丙烯酸在液相中的浓度最小化的手段。

[0692] 连续PPL热分解设计(初级反应器中和初级反应器之外的连续、相等质量流)可使丙烯酸在液相中的浓度最小化，这降低丙烯酸到聚丙烯酸的反应速率(相对于PPL到丙烯酸的反应速率)。从初级反应器的顶部空间去除蒸气将降低在反应器的顶部空间和其液体内容物中的丙烯酸部分压力。优选地不断地使用惰性气体喷射将进一步降低丙烯酸在反应器的液体内容物中的浓度。液体流出物流和任何其它非易失性组分的抽回也可期望用以控制聚丙烯酸的积聚。可将这些流出物流和组分引向第二热分解反应器、到废物处理或到反应性蒸馏以将流中的大量PPL转化为如丙烯酸和短链PPL寡聚物的易失性物种。来自这一蒸馏操作的蒸气流出物可回流到初级反应器，或与来自初级反应器的蒸气流出物相混合。

[0693] 来自各种形式的气相流出物和一定数量合适的热分解反应器优选地(在转到产物存储仓之前)进行冷凝；在冷凝之前以气相形式流过到达蒸馏操作以去除较高沸点和/或较低沸点杂质；转到冷凝，随后以液相形式到达蒸馏以去除较高沸点和/或较低沸点杂质且随后冷凝。在另一实施例中，在存储或直接转到产物存储仓之前，气相流出物在经由蒸馏进行进一步纯化之前在内部冷凝且从非易失性的产物中分离。限制任何液相丙烯酸的温度对于限制聚丙烯酸的产量是已知的。优选地，自由基聚合抑制剂应在所有液相丙烯酸中使用。来自蒸馏操作的底部残留物最优地应返回到初级热分解反应器以用于进一步热分解，但也可排出。

[0694] 在一些变化形式中，热分解过程在氧气和无水大气下操作。举例来说，在某些变化形式中，存在于热分解反应器中的氧气的量少于1wt％、少于0.5wt％、少于0.01wt％或少于0.001wt％。在某些变化形式中存在于热分解反应器中的水的量少于1wt％、少于0.5wt％、少于0.01wt％或少于0.001wt％。

[0695] 冰丙烯酸

[0696] 在一些变化形式中，根据本文中所描述的系统和方法所产生的冰丙烯酸具有至少98％、至少98.5％、至少99％、至少99.1％、至少99.2％、至少99.3％、至少99.4％、至少99.5％、至少99.6％、至少99.7％、至少99.8％或至少99.9％的纯度；或介于99％与99.95％之间、介于99.5％与99.95％之间、介于99.6％与99.95％之间、介于99.7％与99.95％之间或介于99.8％与99.95％之间的纯度。

[0697] 在其它变化形式中，根据本文中所描述的系统和方法所产生的丙烯酸适合于制造高分子量聚丙烯酸。在某些变化形式中，根据本文中所描述的系统和方法所产生的丙烯酸可具有较低纯度，如95％。因此，在一种变化形式中，丙烯酸具有至少95％的纯度。

[0698] 在其它变化形式中，冰丙烯酸具有：

[0699] (i)少于10ppm、少于100ppm、少于500ppm、少于1ppb、少于10ppb或少于100ppb的钴含量；或

[0700] (ii)少于10ppm、少于100ppm、少于500ppm、少于1ppb、少于10ppb或少于100ppb的铝含量；或

[0701] (iii)少于1ppm、少于10ppm、少于100ppm、少于500ppm、少于1ppb或少于10ppb的β-

丙内酯含量；

[0702] (iv)少于2000ppm、少于2500ppm或少于5000ppm的丙烯酸二聚体含量；或

[0703] (v)少于10ppm、少于20ppm、少于50ppm或少于100ppm的水含量，

[0704] 或上述(i)到(v)的任何组合。

[0705] 不同于用以产生冰丙烯酸的已知方法，不产生乙酸、糠醛以及其它呋喃，且因此所述乙酸、糠醛以及其它呋喃不存在于所产生的冰丙烯酸中。

[0706] 冰丙烯酸可用于制造聚丙烯酸，所述聚丙烯酸用于在一次性尿布、训练裤、成人失禁内衣以及卫生巾中的超吸附性聚合物(SAP)。存在于根据本文中的系统和方法所产生的冰丙烯酸中的低含量的杂质有助于促进丙烯酸聚合物(PAA)的高聚合度且避免副产物在最终应用中的不利影响。举例来说，醛杂质在丙烯酸中妨碍聚合且可使已聚合的丙烯酸褪色。顺丁烯二酸酐杂质形成可能对聚合物特性不利的非所要共聚物。羧酸(例如不参与聚合的饱和羧酸)可能影响含PAA或含SAP产物的最终气味且/或损害其使用。举例来说，恶臭气味可能从含有乙酸或丙酸的SAP发出且皮肤刺激可能由含有甲酸的SAP造成。从石油基丙烯酸中降低或去除杂质是成本较高的，无论是生产石油基粗制丙烯酸或是石油基冰丙烯酸。一般来说采用这类成本较高的多阶段蒸馏和/或提取和/或结晶步骤(例如如美国专利第5,705,688号和第6,541,665号中所描述)。

[0707] GAA生产系统/生产方法

[0708] 在一些实施例中，产生系统/产生方法在保持约8000小时的年生产量操作下可产生至少约25千吨每年(“KTA”)冰丙烯酸(“GAA”)、至少约160KTA GAA、至少约250KTA GAA或至少约400KTA GAA。在一些实施例中，生产系统/生产方法可产生至少约2000kg/hr GAA、至少约2500kg/hr GAA、至少约3000kg/hr GAA、至少约3025kg/hr GAA、至少约3500kg/hr GAA、至少约3638kg/hr GAA、至少约4000kg/hr GAA、至少约5000kg/hr GAA、至少约1000kg/hr GAA、至少约20000kg/hr GAA或至少约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生约2000kg/hr GAA、约2500kg/hr PPL、约3000kg/hr GAA、约3500kg/hr GAA、约3638kg/hr GAA、约4000kg/hr GAA、约5000kg/hr GAA、约1000kg/hr GAA、约20000kg/hr GAA或约35000kg/hr GAA。在一些实施例中，生产系统/生产方法可产生介于2000kg/hr GAA与3500kg/hr GAA之间、介于2500kg/hr GAA与3500kg/hr GAA之间、介于约3000kg/hr GAA与3500kg/hr GAA之间、介于2000kg/hr GAA与35000kg/hr GAA之间、介于2500kg/hr GAA与35000kg/hr GAA之间、介于3000kg/hr GAA与35000kg/hr GAA之间、介于3500kg/hr GAA与35000kg/hr GAA之间、介于3638kg/hr GAA与35000kg/hr GAA之间、介于4000kg/hr GAA与35000kg/hr GAA之间、介于5000kg/hr GAA与35000kg/hr GAA之间、介于1000kg/hr GAA与35000kg/hr GAA之间或介于20000kg/hr GAA与35000kg/hr GAA之间。在一些实施例中，生产系统/生产方法可产生至少约25kmol/hr GAA、至少约30kmol/hr GAA、至少约35kmol/hr GAA、至少约40kmol/hr GAA、至少约42kmol/hr或至少约50kmol/hr GAA。GAA产物流的其余部分可包含如丁二酸酐的副反应产物和如THF等剩余溶剂。在一些实施例中，生产系统/生产方法的GAA产物流可具有介于约20到60℃之间介于约30到50℃之间或约40℃的温度。在一些实施例中，生产系统/生产方法的GAA产物流可处在至少约0.5巴、约0.5到1.5巴或至少约1巴的压力下。

[0709] 聚合实例

[0710] 实例1

[0711] 使用丙烯酸钠的作为引发剂的分批bPL聚合

[0712] 在氮气下,向配备有ATR-IR识别指示器的帕尔(Parr)反应器装入16.2mg的丙烯酸钠。将反应器密封并加热到100℃。在50mL不锈钢容器中,在氮气下添加11.8mg的啡噻嗪与25g的β-丙内酯的混合物。将容器密封并连接到反应器。在50psi的CO压力、在100℃下,将β-丙内酯与啡噻嗪的混合物注入到含有丙烯酸钠的反应器中。将反应物搅拌到500rpm,并通过串联IR来监测。在1836cm-1的β-丙酸盐峰值和在1739cm-1的聚(丙内酯)峰值作为时间的函数的曲线展示在图17中。在温度稳定之后,将反应温度设定为145℃。且反应运行5小时,通过这段时间,反应完成。

[0713] 使用CHC13来萃取在反应器中形成的聚合物。通过旋转蒸发仪使挥发物剥离。聚合物在高度真空下进一步干燥以产生21.8g的白色固体。所述固体通过1H、NMR、TGA、SEC以及熔体流变性来分析。所分离固体的SEC产生3710的Mn和8740的Mw。

[0714] 实例2

[0715] 使用四(丁基铵)丙烯酸酯作为引发剂的分批bPL聚合

[0716] 在氮气下,向配备有ATR-IR识别指示器的帕尔(Parr)反应器装入12.2mg的四丁基丙烯酸铵。将反应器密封并加热到100℃。在50mL不锈钢容器中,在氮气下添加25g的β-丙内酯。将容器密封并连接到反应器。在50psi的CO压力、在100℃下,向含有四丁基丙烯酸铵的反应器中注入β-丙内酯。将反应物搅拌到500rpm,并通过串联IR来监测。在1836cm^{-1}的β-丙酸盐峰值和在1739cm^{-1}的聚(丙内酯)峰值作为时间的函数的曲线展示在图21中。在温度稳定之后,将反应温度设定为140℃。在bPL增加之后36分钟时,反应物达到大约89%转化,且在100psi的CO、在140℃下添加25ml的水。在使剩余β-丙内酯水解之后,使用CH_2Cl_2来萃取聚合物。使用旋转蒸发仪去除挥发物且在高度真空下产生17.7g的白色固体。所述固体通过^1H NMR、TGA以及熔体流变性来分析。

[0717] 实例2

[0718] 使用推流式反应器布置的聚合生产

[0719] 将推流式反应器加热到140℃且在环境压力下使用氮气吹扫,所述推流式反应器由1/2″OD X 24 3/4″长且约60mL体积的两个加套的静态混合器、3向氮气/供应口球状阀和具有加套粘度计(具有372传感器的Cambridge Viscosity ViscoPro 2000)的出口、K型热电偶、ATIR IR探针(Mettler-Toledo DS AgX CompTM和ReactIRTM 15)以及0到250psig背压调整器组成。通过使0.1670g的丙烯酸钠(研磨,筛分到100目且在真空下在130℃下干燥,0.001776mol)、0.1536g啡噻嗪以及670mL的□-丙内酯(约760g,10.6摩耳,冷却到-20℃)在于手套箱中配备有磁性搅拌棒的一升、额定压力/真空GL45瓶中合并来制备供应混合物。所述瓶密闭有配备有汲取管和在一个通口上的2向1/8″球状阀、在第二通口上具有1psi裂解压力检查阀的1/8″2向球状阀以及具有安装在第三通口上的Luer锁的1/8″三向球状阀的三通GL45盖。简单地搅拌混合物以使啡噻嗪溶解且使丙烯酸钠悬浮。将密封瓶从手套箱中去除,运送到推流式反应器,沉浸在电磁搅拌器上方的水/冰池中,且经由三个1/8″压缩配件分别连接到供应泵、排气线路(到充满2%硫酸的洗涤器)以及氮针阀。以400rpm搅拌混合物以保持丙烯酸钠悬浮。2向排气阀门打开,随后将3向氮/注入阀从对氮气关闭切换且调节氮针阀以在洗涤器中的得到气泡状稳定流。供应阀随后打开,接着打开位于供应泵(Eldex

Optos 2SM,0.01到10.00mL/min)上的充装阀且以5.00mL/min的流动速率接通泵且允许运行直到(Teflon FEP)从充装通口到洗涤器的直线显示全部气泡已排出。随后断开泵,流动设定为0.50mL/min,充装/供应3向球状阀切换为供应,反应器入口三向球状阀从氮气切换为供应且所述泵变回为接通。

[0720] 在4小时之后,反应器出口背压调整器从环境压力调整到200psig,且接通粘度计和ReactIR两者。在另外一个半小时之后,反应器完全地加压,粘度计(70cP,补偿到120℃)和ReactIR(约95%转化)读数稳定且产物被收集到含有300mL的磁性搅拌水的一升收集瓶中。在另外22.5小时之后,供应混合物几乎排空且经由注射器和安装在氮气/填充3向球状阀上的Luer锁将三氯甲烷的20mL部分添加到供应瓶。当供应瓶几乎再次排空时,添加另外20mL的三氯甲烷。当电荷已耗尽时,添加另外500mL的三氯甲烷。将新鲜接收瓶放置在反应器出口上且当供应泵和循环池断开时将条件再维持21小时。

[0721] 将来自第一接收器瓶的粗产物混合物运送到具有额外500mL的水的大型掺混机,掺混直到未观察到有粒子>5mm且通过过滤来收集固体,风干且随后在40℃下真空干燥20小时以得到562.1克的固体PPL产物。使三氯甲烷中的PPL溶液与来自第二接收器瓶的水性液体的混合物分离,使用水洗涤三氯甲烷相,干燥且通过共沸蒸馏浓缩到300mL且在600mL的2-丙醇中稀释。所得沉淀通过过滤来收集,风干且随后在40℃下在真空中干燥2小时以得到90.5克的无色固体PPL产物。在50℃下,在旋转式汽化器上使滤液剥离挥发物以得到45.0g的清澈、无色油状物,所述油状物在冷却时分离成液体和固体。

[0722] 1H NMR分析表明来自第一接收器的固体由556克的PPL组成,其中分子量约1210g/mol,具有由bPL在水中的水解所产生的少量(6克)的3-羟基丙酸(3-HPA)(GPC结果显示Mn=275,Mw=1530且Mn/Mw=5.56)。从第二接收器中分离的固体含有90克的PPL,其中分子量2030g/mol(GPC结果显示Mn=328,Mw=1900,Mw/Mn=5.79。)且具有0.5克的3-HPA。

[0723] 聚合实例

[0724] 实例4

[0725] PPL到丙烯酸的分批热分解

[0726] 实施由25mL近似内部体积的二颈圆底玻璃烧瓶(反应烧瓶)组成的实验室规模分批热分解系统。反应烧瓶配备有内部热电偶且烧瓶中的顶部中心开口配备有短路径蒸馏装置。短路径蒸馏装置由具有用以监测蒸气温度的额外热电偶的短路径釜(类似于Ace Glass条目#6554-06)组成,后接水冷式冷凝器,且最后是干冰/丙酮冷却杜瓦瓶中的四臂“母牛”产物接收器。反应烧瓶设定在织物加热套中,所述织物加热套的能量通过从位于反应烧瓶内部的热电偶接收反馈的温度控制器来控制。额外热量使用电热带来提供,所述电热带缠绕在反应烧瓶和蒸馏装置的顶部周围。反应烧瓶的顶部和蒸馏装置的底部是隔热的。织物加热套设定在磁性搅拌板上方,且将PTFE涂覆搅拌棒添加到反应烧瓶。

[0727] 向配衡反应烧瓶装入90mg无水丙烯酸钠、5mg PTZ以及由不含溶剂的bPL的开环聚合在丙烯酸钠(浓度为1mol每6,000mol bPL)和啡噻嗪(在bPL中浓度为200ppmw)的存在下所产生的4.995g的PPL。另外,配衡产物接收器预装载有5mg PTZ(分布在四个产物臂当中)。在系统组件之后,产物接收器附接到氮气源和真空源上,且使用氮气置换空气。随后,将反应器内容物加热到90摄氏度直到熔融且开始搅拌。在真空下,将系统引入到大约700torr的绝对压力下,且将反应器温度设定点设定为210摄氏度。在数分钟内在反应烧瓶内部观察到

内部回流。加热反应器内容物直到210摄氏度耗时8到10分钟。将反应器内容物达到210摄氏度的时刻定义为t＝0。使反应器内容物保持在210摄氏度保持10分钟，在这个时间点，除了玻璃态较暗固体和搅拌棒之外，反应器烧瓶大部分排空。

[0728] 稍后确定称重为156mg的反应烧瓶中的残余材料。当热源关闭时，获得四个产物样品——含有直到t＝2分钟所收集的材料的129到098A、含有介于t＝2分钟与t＝8分钟之间收集的材料的129到098B、含有介于t＝8分钟与t＝9分钟之间的材料的129到098C以及含有介于t＝9分钟与t＝10分钟之间所收集材料的129到098D。所收集的总体产物称重为4.7816g。随后，将每一样品从母牛移液到标记小瓶，且采集样品以用于1H NMR(参见图25到28)。NMR分析表明平均丙烯酸含量在129到098A中为94.4质量％、在129到098B中为90.7质量％、在129到098C中为90.6质量％且在129到098D中为92.5质量％。其余部分由双丙烯酸酯和痕量的其它PPL寡聚物组成，其中n>2。

[0729] 聚合实例

[0730] 实例4

[0731] PPL到丙烯酸的分批热分解

[0732] 由50mL近似内部体积的二颈圆底玻璃烧瓶(反应烧瓶)组成的实验室规模分批热分解系统。反应烧瓶配备有内部热电偶且烧瓶中的顶部中心开口配备有蒸馏装置。蒸馏设备由共轴定向串联的韦氏分馏柱(Vigreux columns)组成(每一个类似于Ace Glass条目#6578-04)，后接具有用以监测蒸气温度的额外热电偶的转接器，后接水冷式冷凝器，且最后是干冰/丙酮冷却杜瓦瓶中的50mL圆底产物接收器。反应烧瓶设定在织物加热套中，所述织物加热套的能量通过从位于反应烧瓶内部的热电偶接收反馈的温度控制器来控制。额外热量使用电热带来提供，所述电热带缠绕在反应烧瓶和蒸馏装置的顶部周围。反应烧瓶的顶部和蒸馏装置的底部是隔热的。织物加热套设定在磁性搅拌板上方，且将PTFE涂覆搅拌棒添加到反应烧瓶。

[0733] 向配衡反应烧瓶装入1000mg无水丙烯酸钠、20mg PTZ以及由不含溶剂的bPL的开环聚合在丙烯酸钠(浓度为1mol每6,000mol bPL)和啡噻嗪(在bPL中浓度为200ppmw)的存在下所产生的19.162g的PPL。另外，配衡产物接收器预装载有5mg PTZ。在系统组件之后，产物接收器附接到氮气源和真空源上，且使用氮气置换空气。随后，将反应器内容物加热到90摄氏度直到熔融且开始搅拌。在真空下，将系统引入到大约90torr的绝对压力下，且将反应器温度设定点设定为165摄氏度。在数分钟内在反应烧瓶内部观察到内部回流。加热反应器内容物直到165摄氏度耗时大约10分钟。将反应器内容物达到165摄氏度的时刻定义为t＝0。反应器内容物保持在165摄氏度下40分钟，在这个时间点，反应器烧瓶仍易于通过搅拌棒来混合。

[0734] 稍后确定称重为4.7186g的反应烧瓶中的残余材料。产物样品129到108由全部所收集产物组成，且称重为14.6586g。随后，采集样品以用于1H NMR(参见图29)。NMR分析表明129到108_Dist中的平均丙烯酸含量为99.7％。其余部分由双丙烯酸酯和痕量的其它PPL寡聚物组成，其中n>2。

[0735] 本申请案在文本和图式中揭示若干数值范围。尽管并未在说明书中完全陈述确切范围限制，然而所揭示的数值范围本质上支持在本揭示数值范围内的任何范围或值，因为本发明可贯穿本揭示数值范围而实施。

[0736] 呈现上文描述，使得本领域的普通技术人员能够作出并使用本发明，且上文描述在特定应用的上下文和其需求中提供。本领域的技术人员将易于清楚对优选实施例的各种修改，并且在不脱离本发明的精神和范畴的情况下，本文中所定义的一般原理可应用于其它实施例和应用。因此，本文中所描述的系统和方法并不希望受限于所展示的具体实施例，而应被赋予与本文中所揭示的原理和特征相一致的最广范围。最后，在本申请案中所参考的专利和公开案的全部揭示由此以参考方式并入本文中。

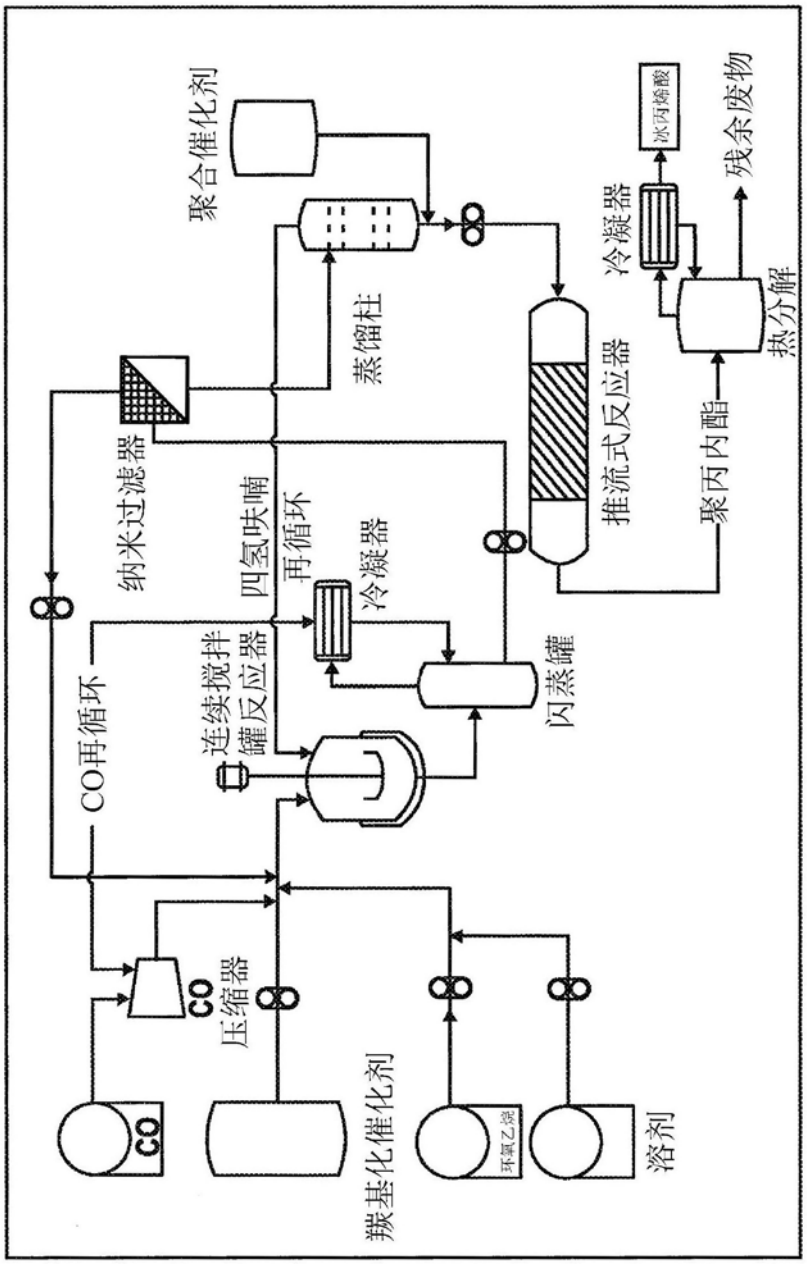

聚合催化剂
蒸馏柱
冷凝器
冰丙烯酸
残余废物
热分解
聚丙内酯
推流式反应器
闪蒸罐
纳米过滤器
四氢呋喃
再循环
冷凝器
连续搅拌
罐反应器
CO再循环
CO
压缩器
羰基化催化剂
环氧乙烷
溶剂

图1

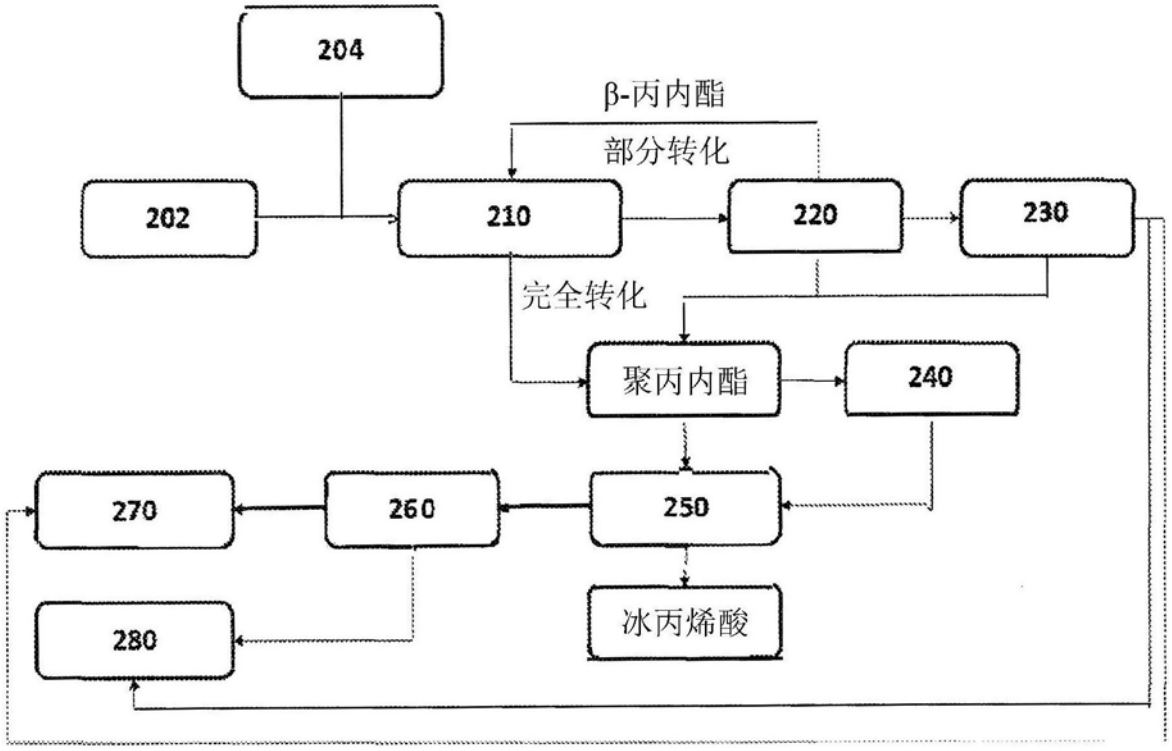

204
β-丙内酯
部分转化
202
210
220
230
完全转化
聚丙内酯
240
270
260
250
冰丙烯酸
280

图2

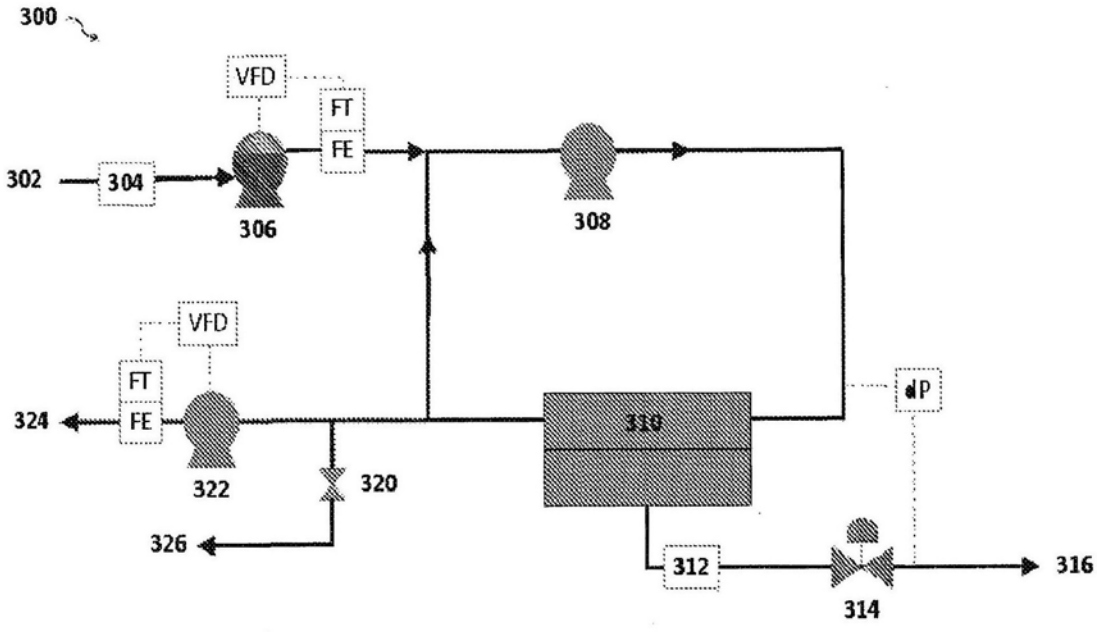

300
VFD
FT
FE
302
304
306
308
VFD
FT
FE
324
322
320
326
310
dP
312
314
316

图3

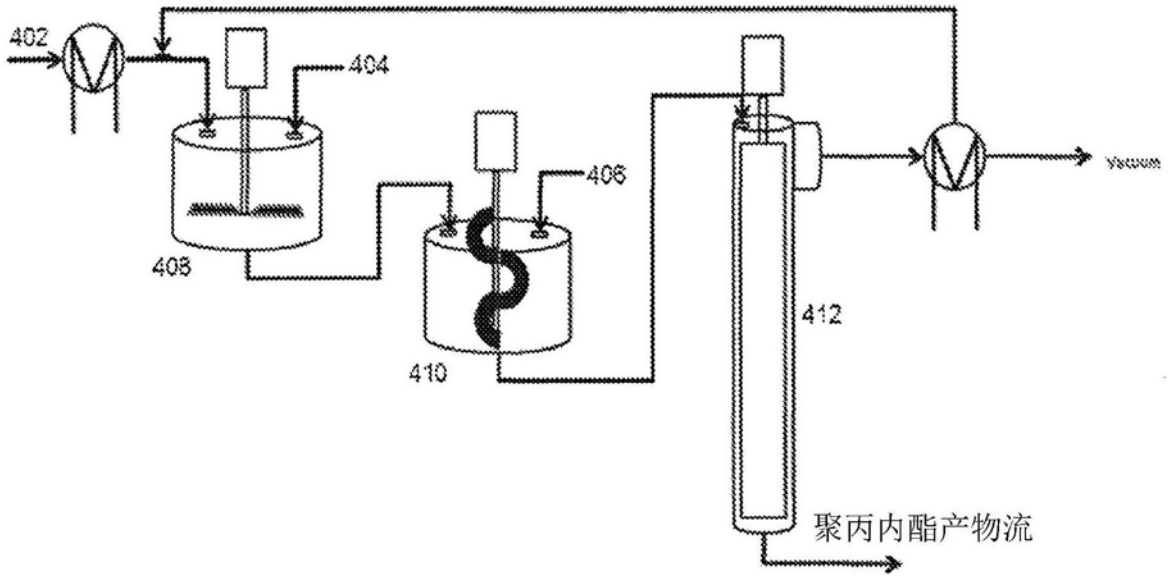

402
404
406
408
410
412
聚丙内酯产物流

图4A

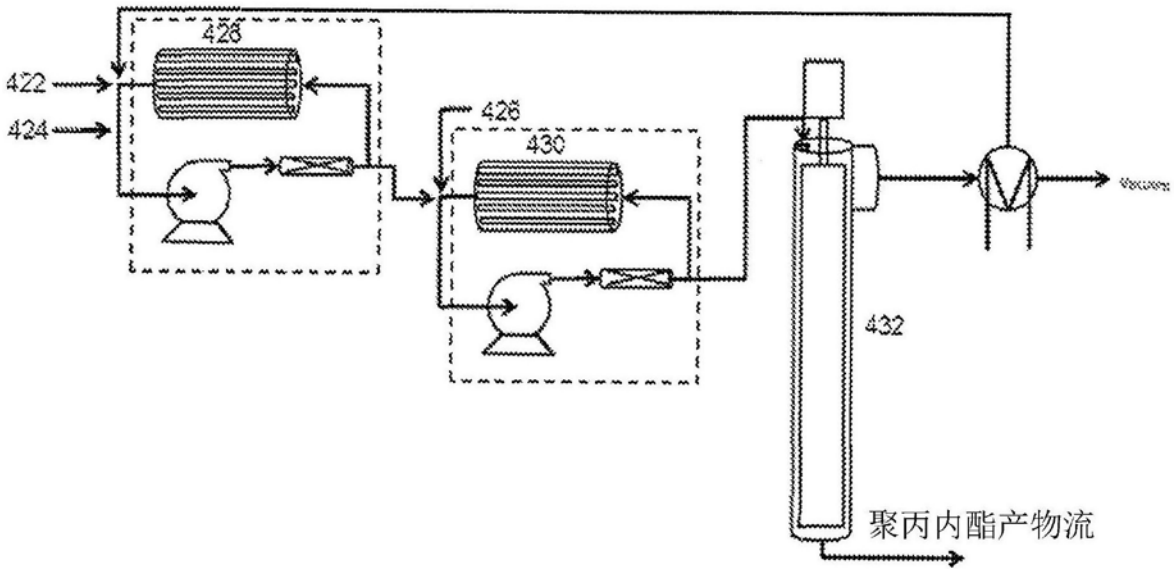

422
424
426
426
430
432
聚丙内酯产物流

图4B

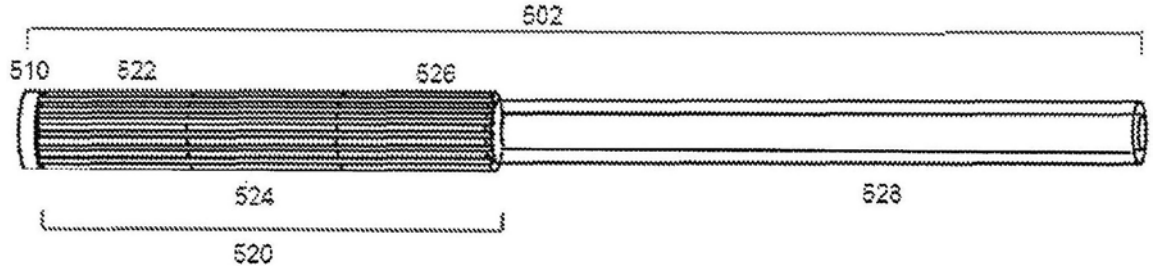

502
510
522
526
524
528
520

图5

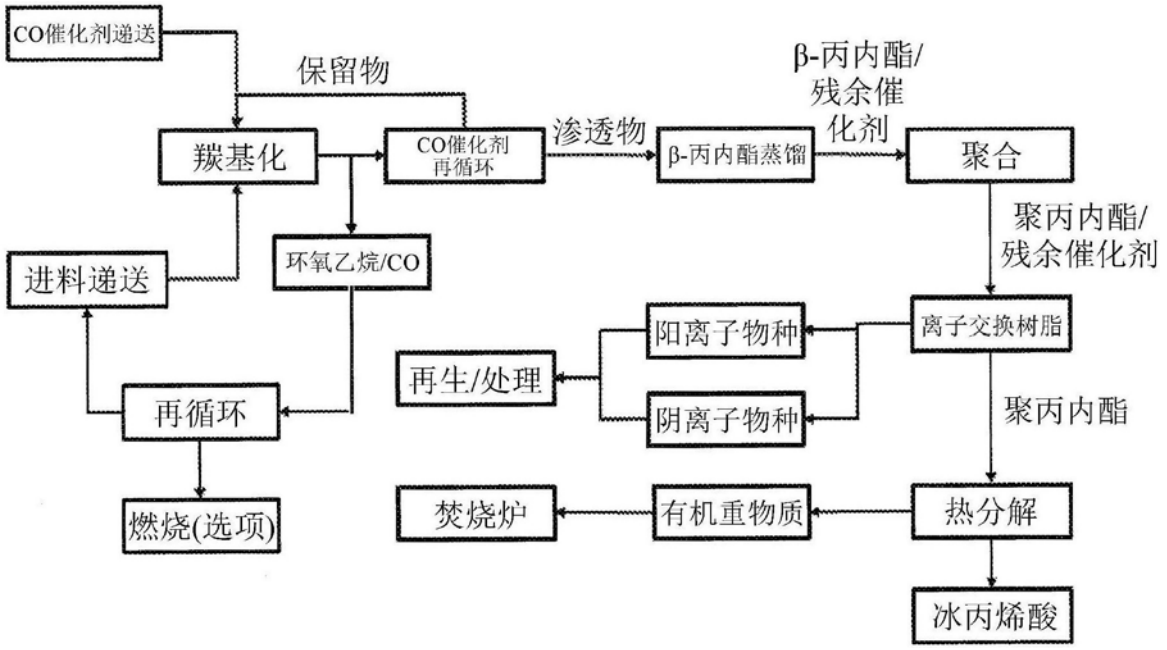

CO催化剂递送
保留物
羰基化
CO催化剂再循环
渗透物
β-丙内酯蒸馏
β-丙内酯/残余催化剂
聚合
聚丙内酯/残余催化剂
进料递送
环氧乙烷/CO
离子交换树脂
阳离子物种
再生/处理
阴离子物种
聚丙内酯
再循环
燃烧(选项)
焚烧炉
有机重物质
热分解
冰丙烯酸

图6

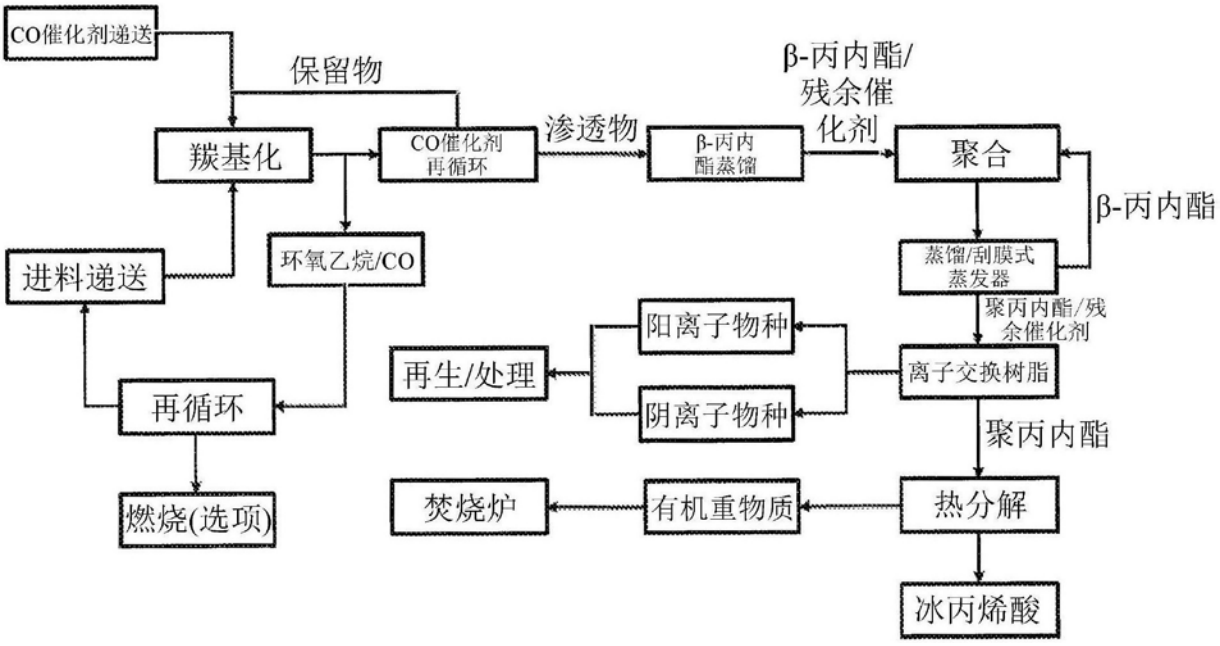

CO催化剂递送
保留物
羰基化
CO催化剂再循环
渗透物
β-丙内酯蒸馏
β-丙内酯/残余催化剂
聚合
β-丙内酯
进料递送
环氧乙烷/CO
蒸馏/刮膜式蒸发器
聚丙内酯/残余催化剂
阳离子物种
再生/处理
离子交换树脂
阴离子物种
聚丙内酯
再循环
燃烧(选项)
焚烧炉
有机重物质
热分解
冰丙烯酸

图7

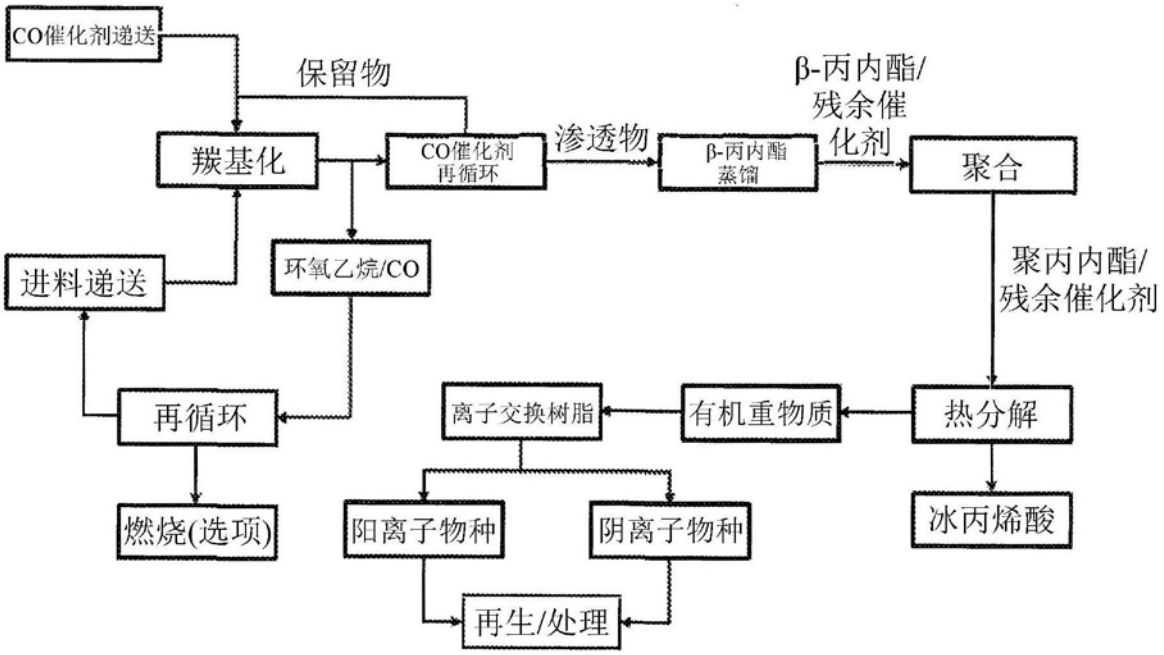

CO催化剂递送
保留物
羰基化
CO催化剂再循环
渗透物
β-丙内酯蒸馏
β-丙内酯/残余催化剂
聚合
进料递送
环氧乙烷/CO
聚丙内酯/残余催化剂
再循环
离子交换树脂
有机重物质
热分解
燃烧(选项)
阳离子物种
阴离子物种
冰丙烯酸
再生/处理

图8

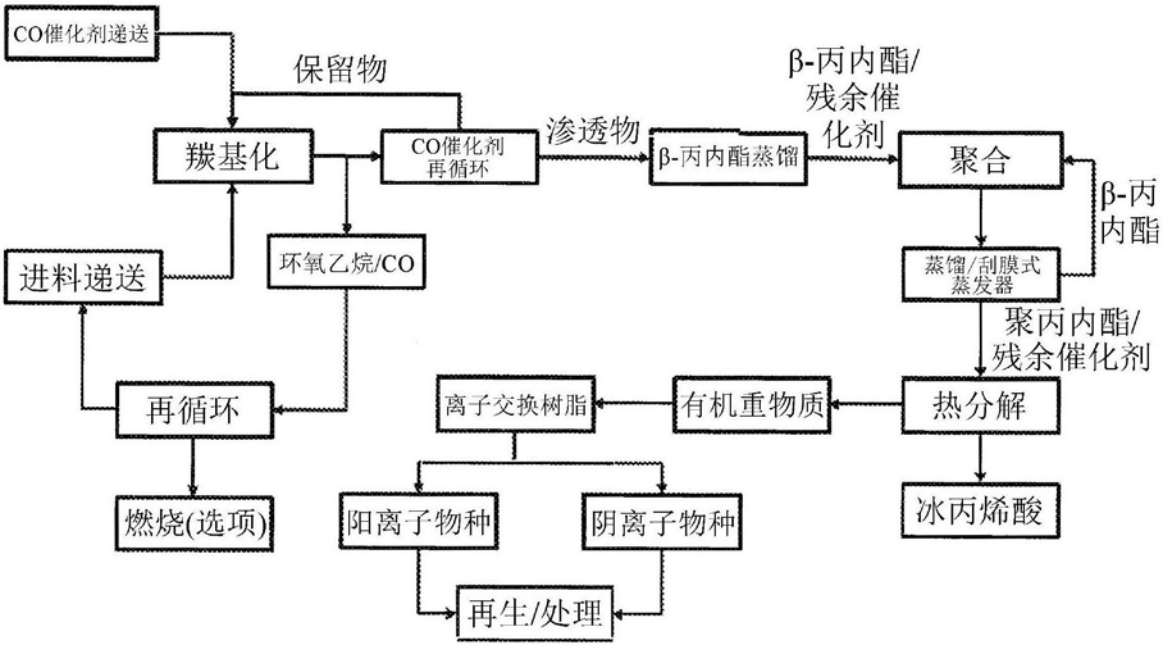

CO催化剂递送
保留物
羰基化
CO催化剂再循环
渗透物
β-丙内酯蒸馏
β-丙内酯/残余催化剂
聚合
β-丙内酯
进料递送
环氧乙烷/CO
蒸馏/刮膜式蒸发器
聚丙内酯/残余催化剂
再循环
离子交换树脂
有机重物质
热分解
燃烧(选项)
阳离子物种
阴离子物种
冰丙烯酸
再生/处理

图9

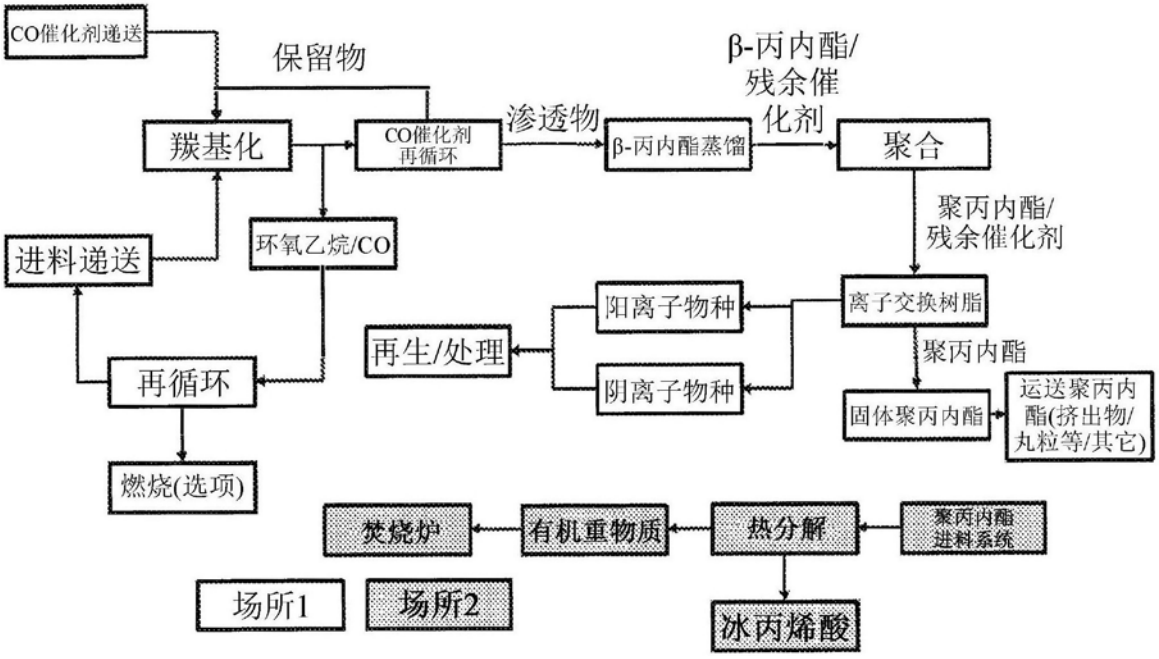

CO催化剂递送
保留物
β-丙内酯/
残余催
化剂
羰基化
CO催化剂
再循环
渗透物
β-丙内酯蒸馏
聚合
聚丙内酯/
残余催化剂
进料递送
环氧乙烷/CO
阳离子物种
离子交换树脂
再生/处理
聚丙内酯
再循环
阴离子物种
固体聚丙内酯
运送聚丙内
酯(挤出物/
丸粒等/其它)
燃烧(选项)
焚烧炉
有机重物质
热分解
聚丙内酯
进料系统
场所1
场所2
冰丙烯酸

图10

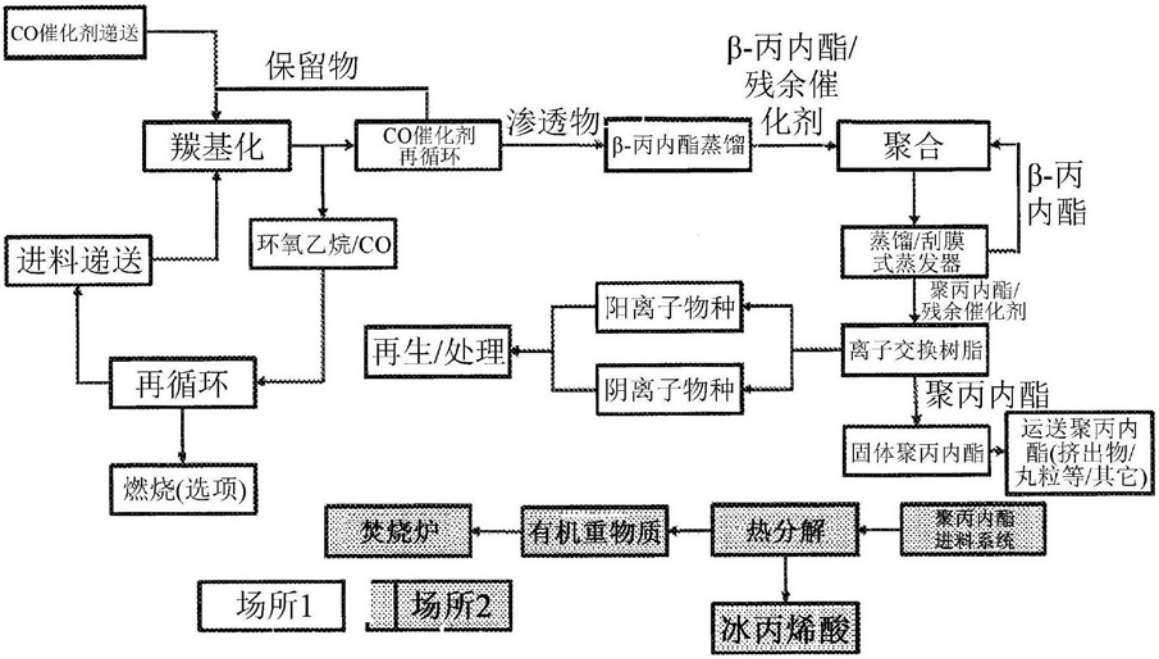

CO催化剂递送
保留物
β-丙内酯/
残余催
化剂
羰基化
CO催化剂
再循环
渗透物
β-丙内酯蒸馏
聚合
β-丙
内酯
进料递送
环氧乙烷/CO
蒸馏/刮膜
式蒸发器
聚丙内酯/
残余催化剂
阳离子物种
再生/处理
离子交换树脂
再循环
阴离子物种
聚丙内酯
固体聚丙内酯
运送聚丙内
酯(挤出物/
丸粒等/其它)
燃烧(选项)
焚烧炉
有机重物质
热分解
聚丙内酯
进料系统
场所1
场所2
冰丙烯酸

图11

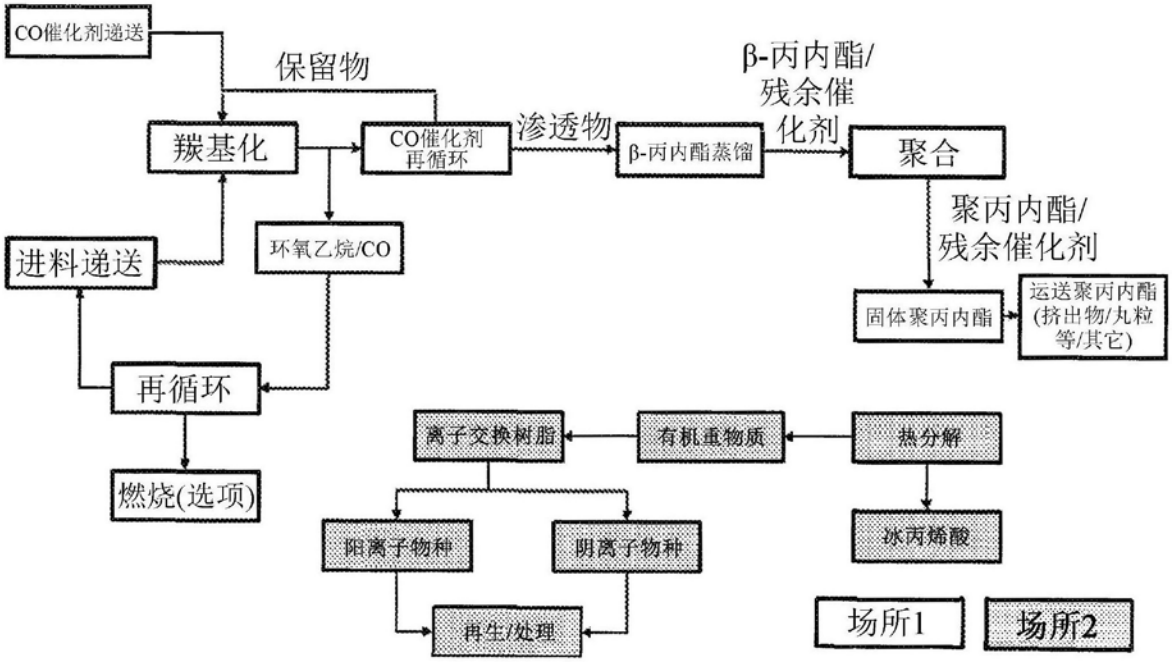

CO催化剂递送
保留物
羰基化
CO催化剂再循环
渗透物
β-丙内酯蒸馏
β-丙内酯/残余催化剂
聚合
聚丙内酯/残余催化剂
进料递送
环氧乙烷/CO
固体聚丙内酯
运送聚丙内酯(挤出物/丸粒等/其它)
再循环
燃烧(选项)
离子交换树脂
有机重物质
热分解
阳离子物种
阴离子物种
冰丙烯酸
再生/处理
场所1
场所2

图12

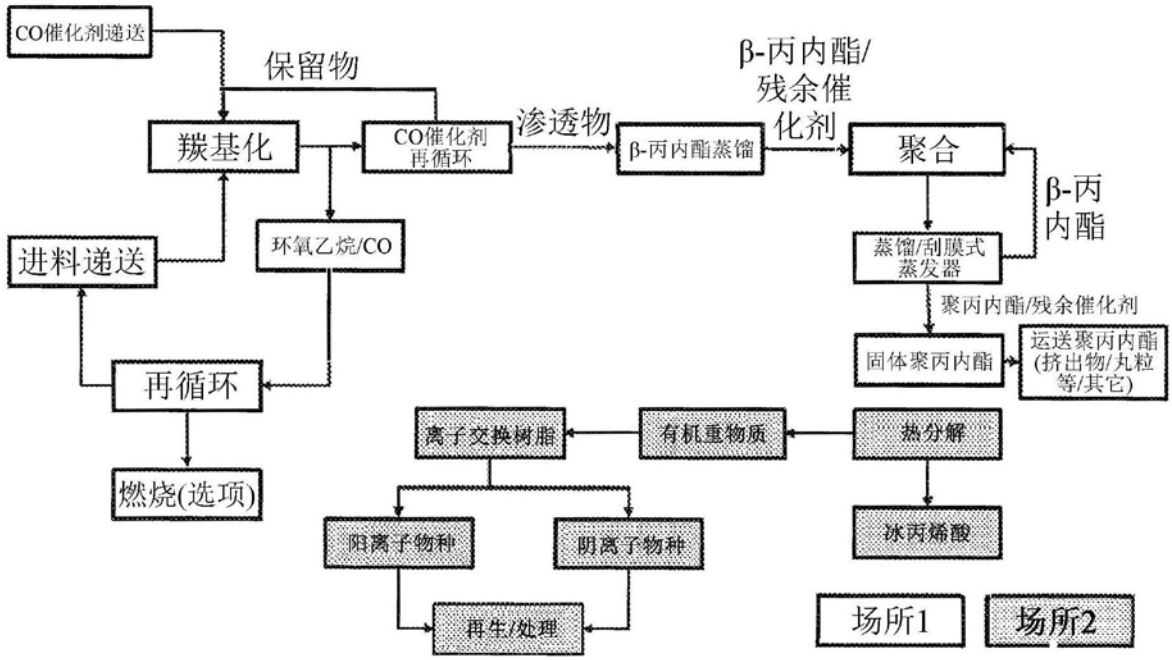

CO催化剂递送
保留物
羰基化
CO催化剂再循环
渗透物
β-丙内酯蒸馏
β-丙内酯/残余催化剂
聚合
β-丙内酯
进料递送
环氧乙烷/CO
蒸馏/刮膜式蒸发器
聚丙内酯/残余催化剂
固体聚丙内酯
运送聚丙内酯(挤出物/丸粒等/其它)
再循环
燃烧(选项)
离子交换树脂
有机重物质
热分解
阳离子物种
阴离子物种
冰丙烯酸
再生/处理
场所1
场所2

图13

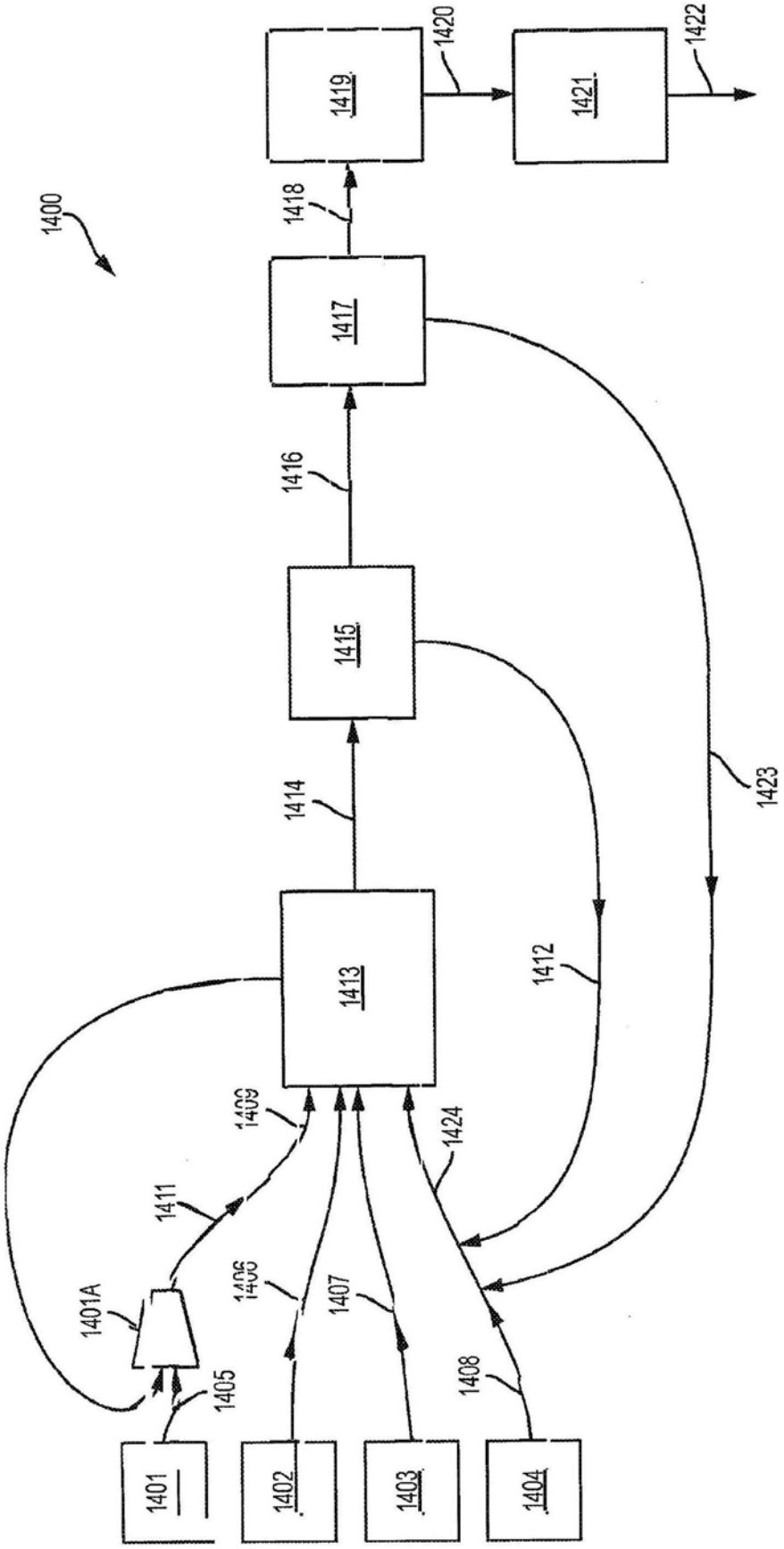

1400
1401
1401A
1402
1403
1404
1405
1407
1408
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424

图14

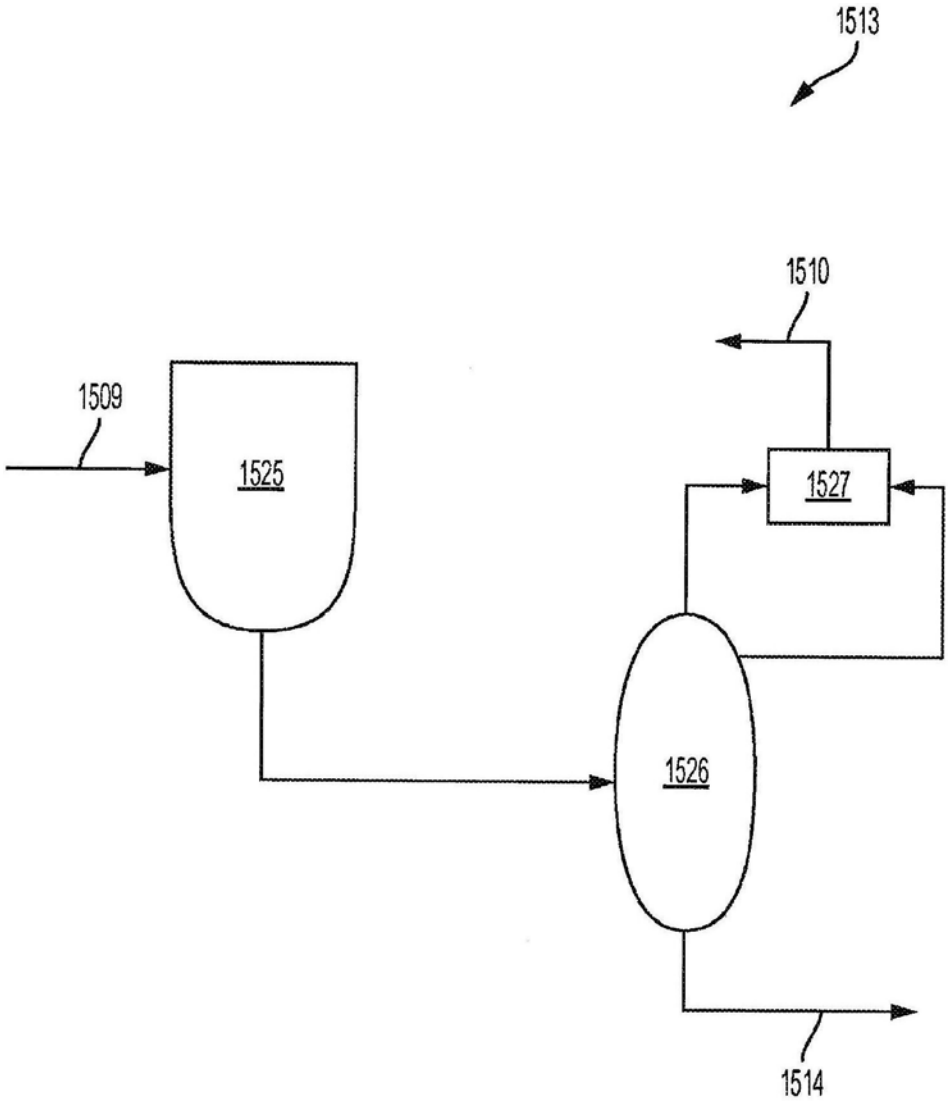


图15

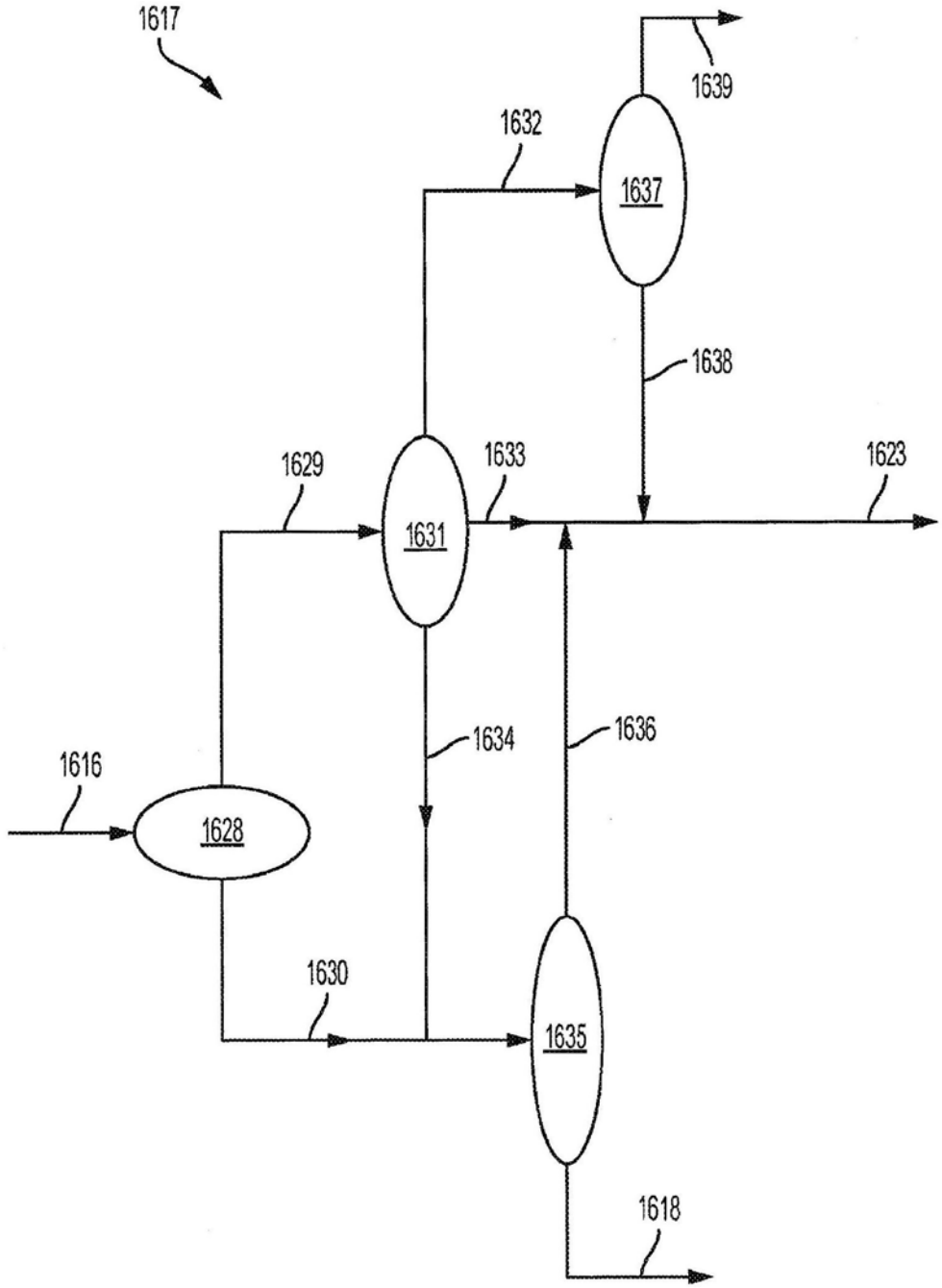

1617
1639
1632
1637
1638
1629
1633
1623
1631
1634
1636
1616
1628
1630
1635
1618

图16

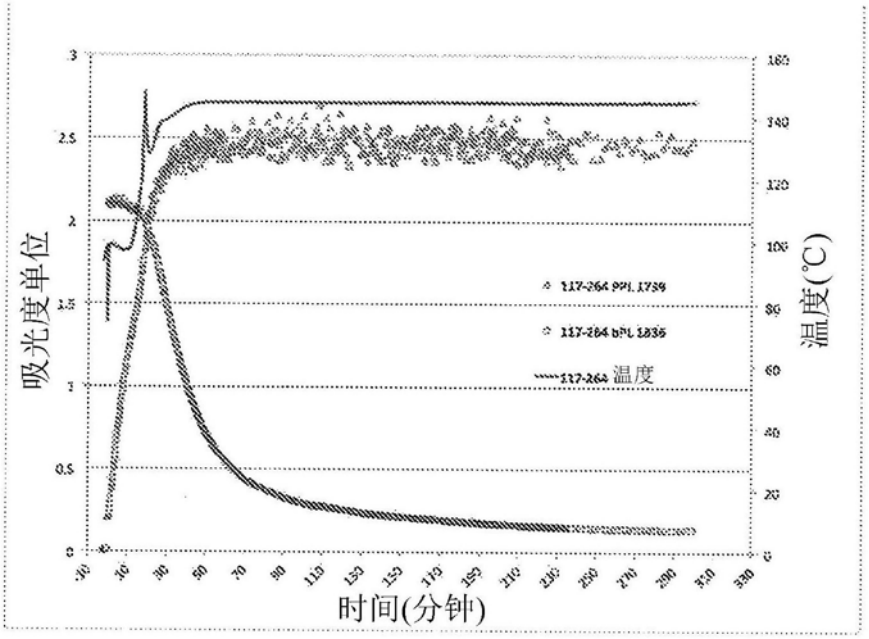


图17

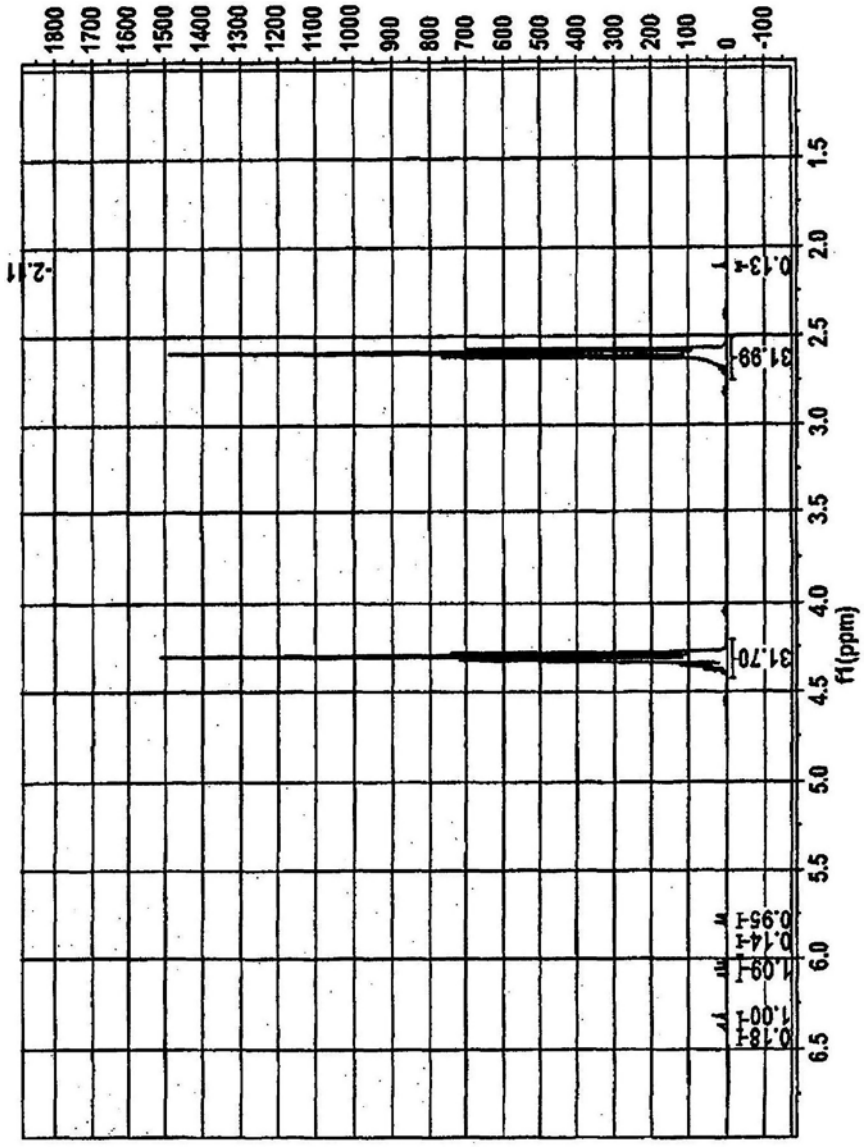

1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1(ppm)
-2.11
0.13-1
31.98
31.70
0.95-1
0.14-1
1.09-1
1.00-1
0.18-1

图18

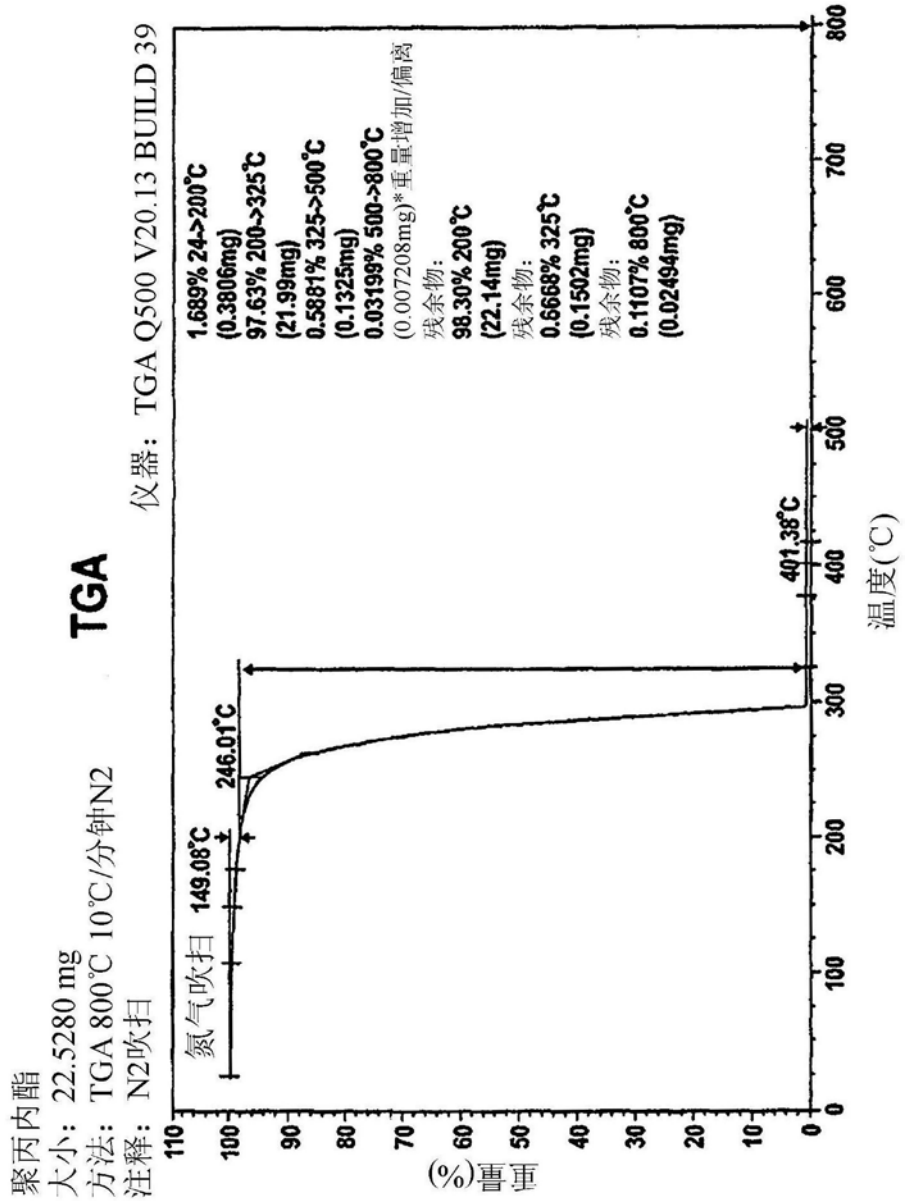

聚丙内酯
大小： 22.5280 mg
方法： TGA 800℃ 10℃/分钟N2
注释： N2吹扫
TGA
仪器： TGA Q500 V20.13 BUILD 39
氮气吹扫
149.08℃
246.01℃
401.38℃
1.689% 24->200℃
(0.3806mg)
97.63% 200->325℃
(21.99mg)
0.5881% 325->500℃
(0.1325mg)
0.03199% 500->800℃
(0.007208mg)*重量增加/偏离
残余物：
98.30% 200℃
(22.14mg)
残余物：
0.6668% 325℃
(0.1502mg)
残余物：
0.1107% 800℃
(0.02494mg)
重量(%)
温度(℃)

图19

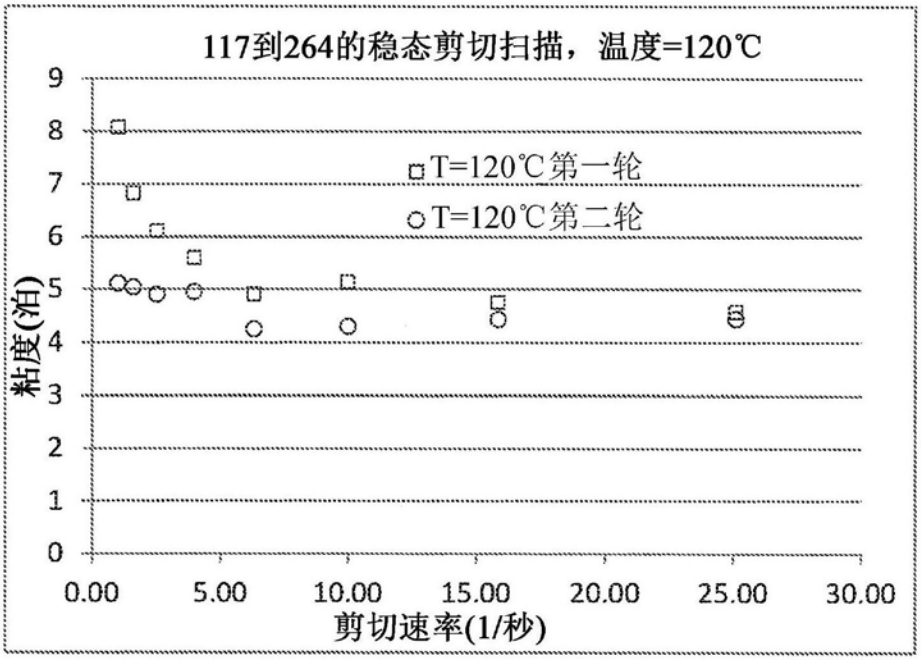

117到264的稳态剪切扫描，温度=120℃
T=120℃第一轮
T=120℃第二轮
粘度(泊)
剪切速率(1/秒)
0
1
2
3
4
5
6
7
8
9
0.00
5.00
10.00
15.00
20.00
25.00
30.00

图20

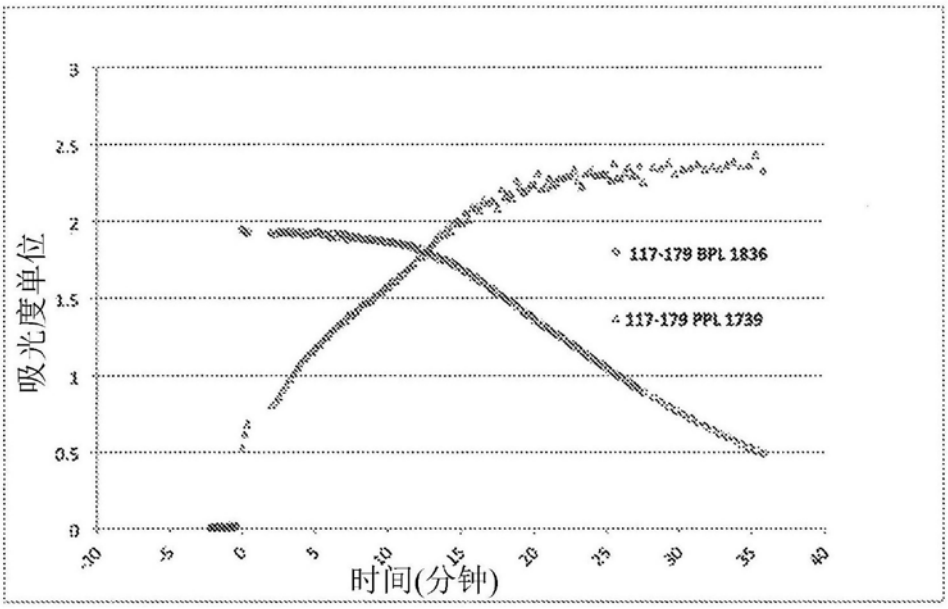

吸光度单位
时间(分钟)
117-179 BPL 1836
117-179 PPL 1739

图21

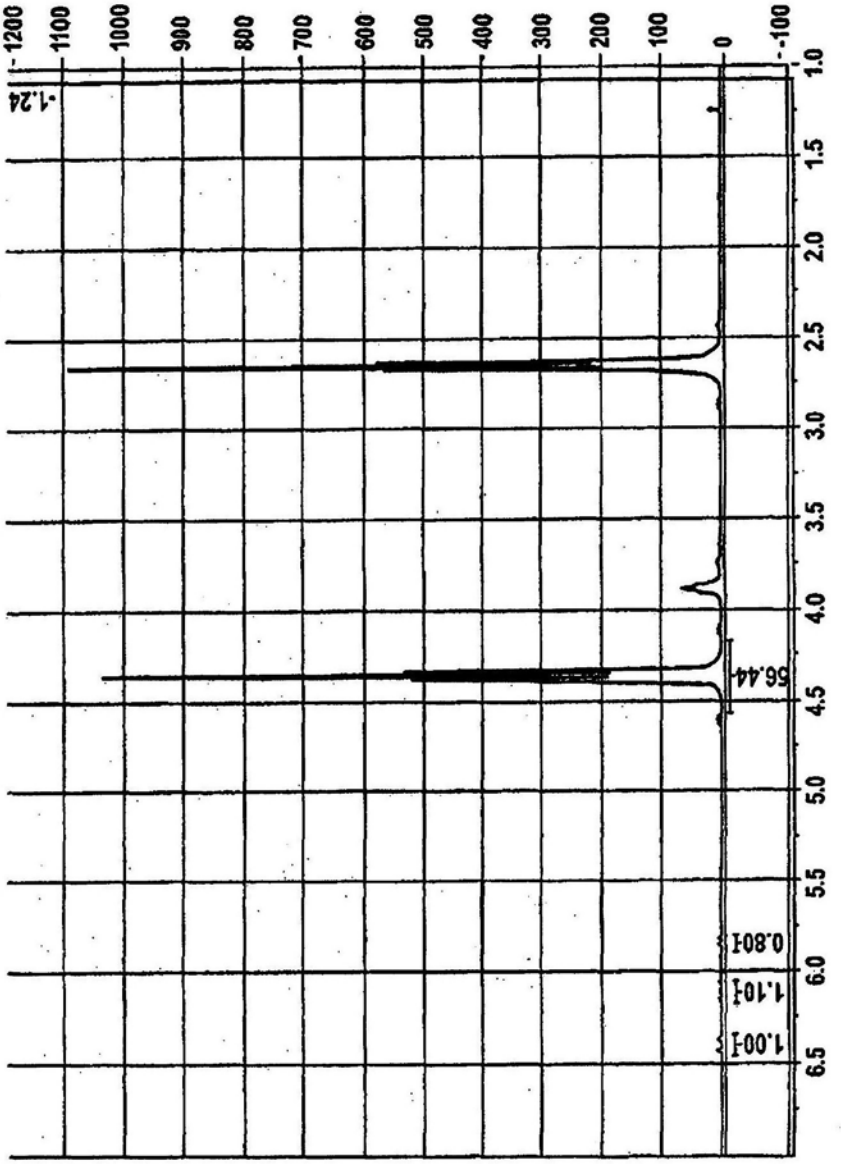

1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
-1.24
56.44
0.80
1.10
1.00

图22

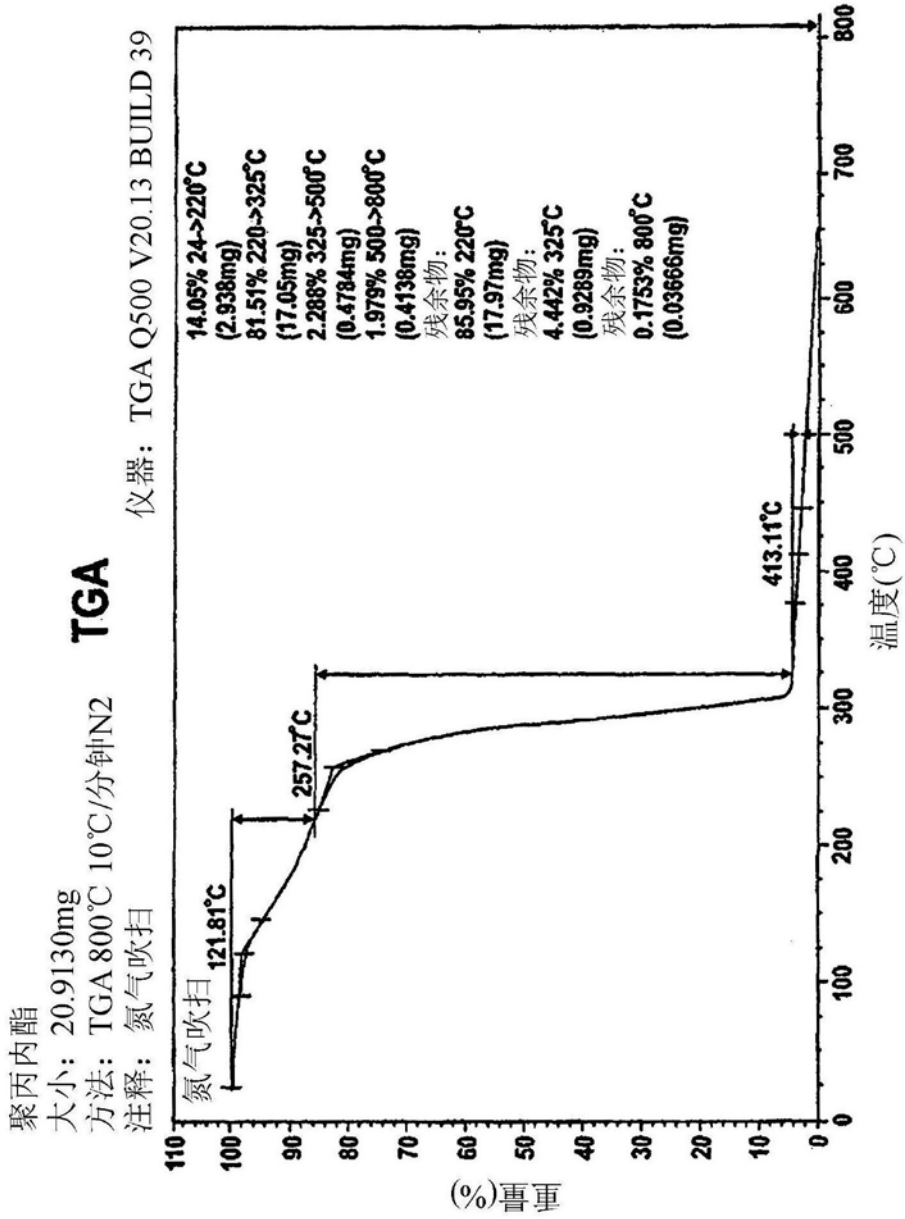

聚丙内酯
大小：20.9130mg
方法：TGA 800℃ 10℃/分钟N2
注释：氮气吹扫
TGA
仪器：TGA Q500 V20.13 BUILD 39
氮气吹扫
121.81℃
257.27℃
413.11℃
14.05% 24->220℃
(2.938mg)
81.51% 220->325℃
(17.05mg)
2.288% 325->500℃
(0.4784mg)
1.979% 500->800℃
(0.4138mg)
残余物：
85.95% 220℃
(17.97mg)
残余物：
4.442% 325℃
(0.9289mg)
残余物：
0.1753% 800℃
(0.03666mg)
重量(%)
温度(℃)

图23

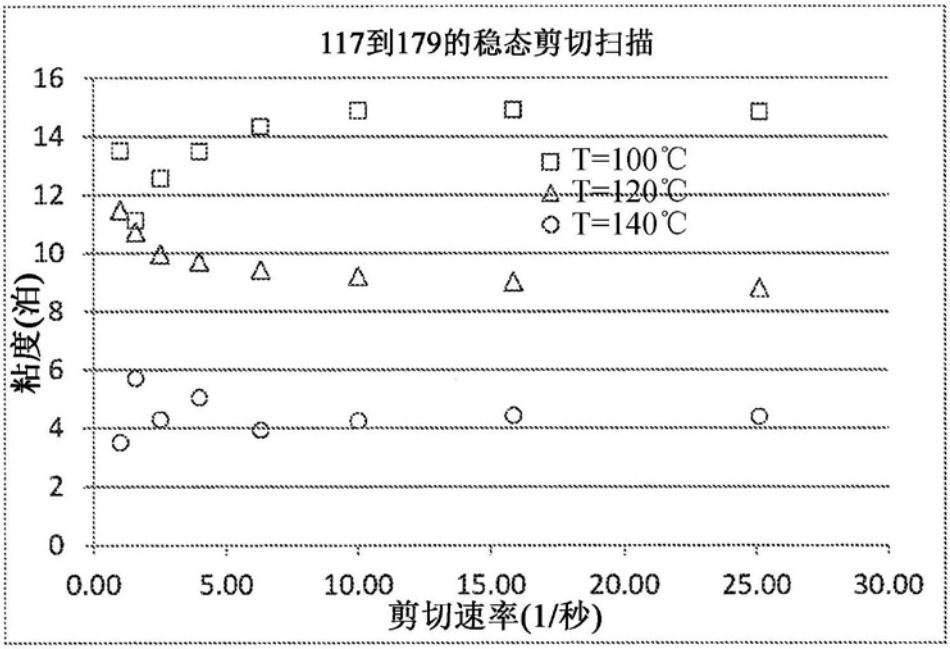

117到179的稳态剪切扫描
粘度(泊)
剪切速率(1/秒)
T=100℃
T=120℃
T=140℃
0
2
4
6
8
10
12
14
16
0.00
5.00
10.00
15.00
20.00
25.00
30.00

图24

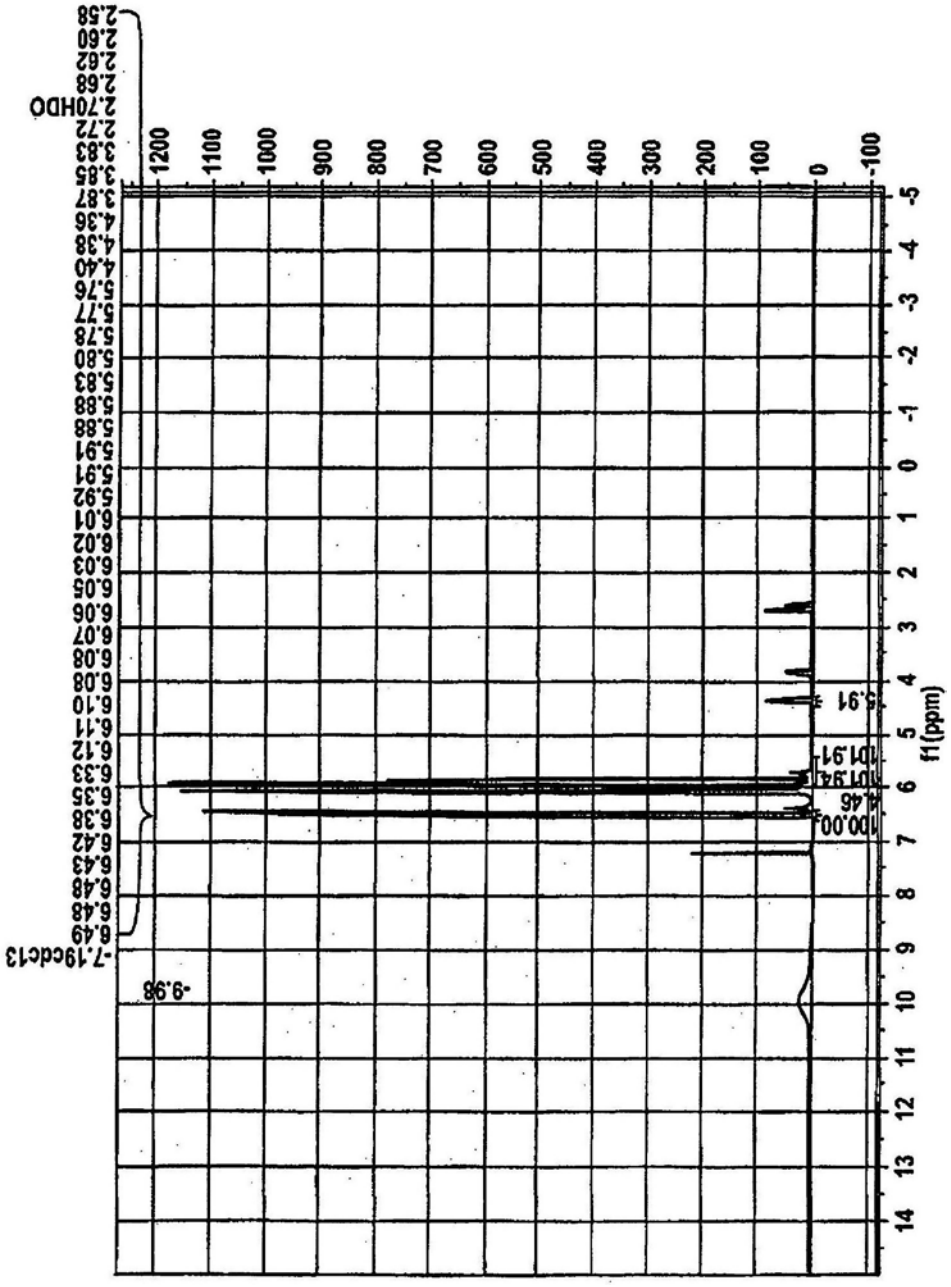


图25

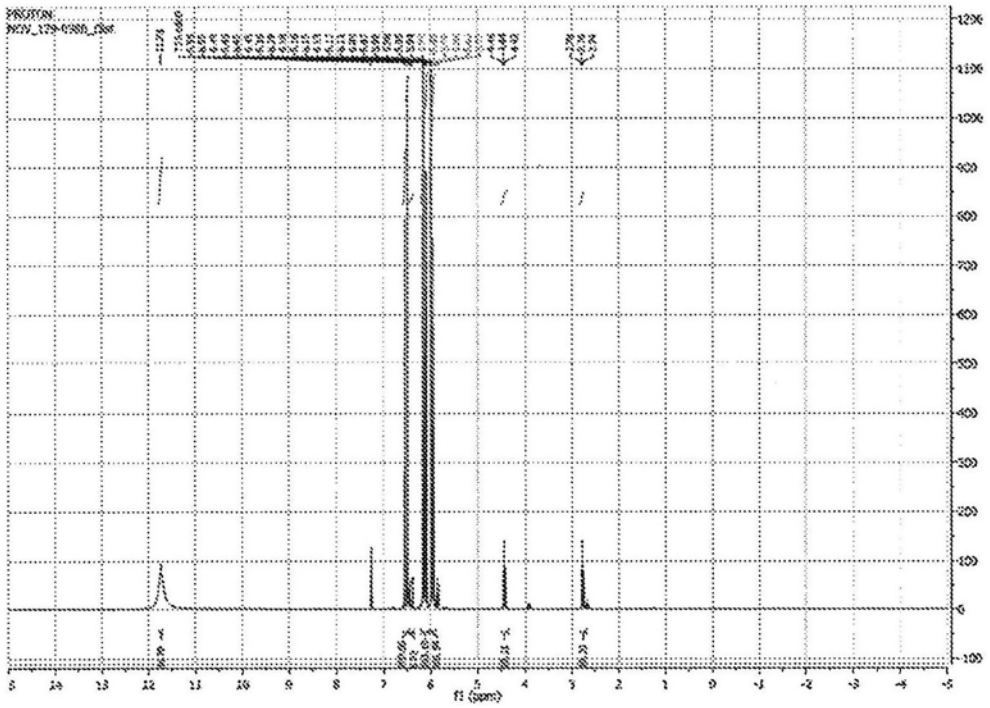


图26

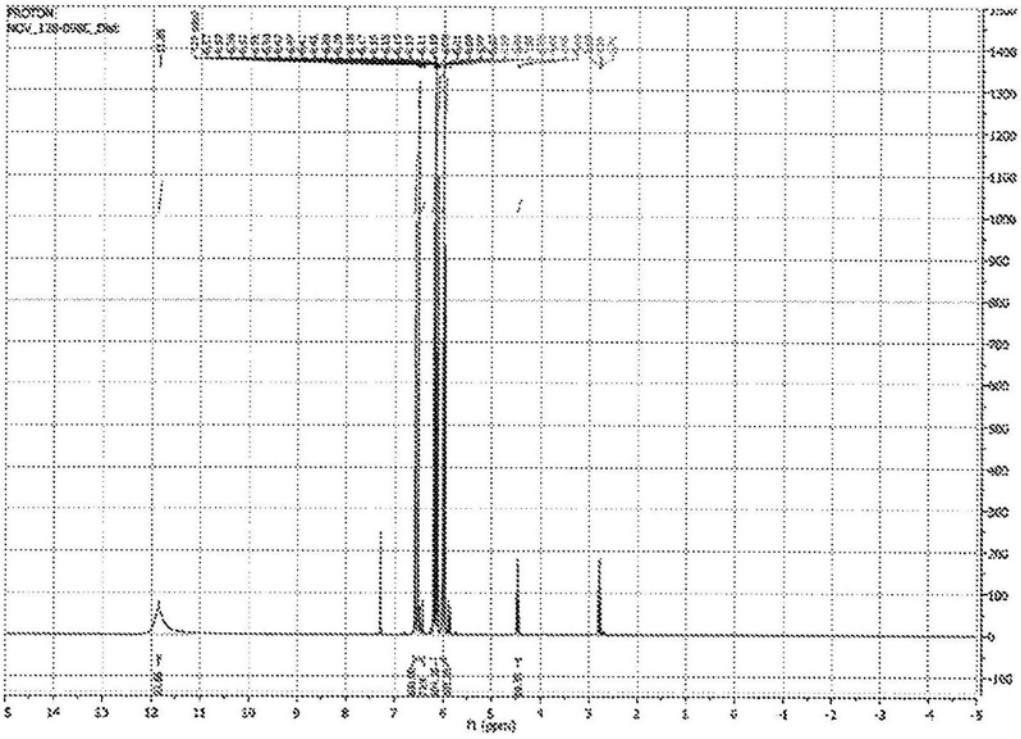


图27

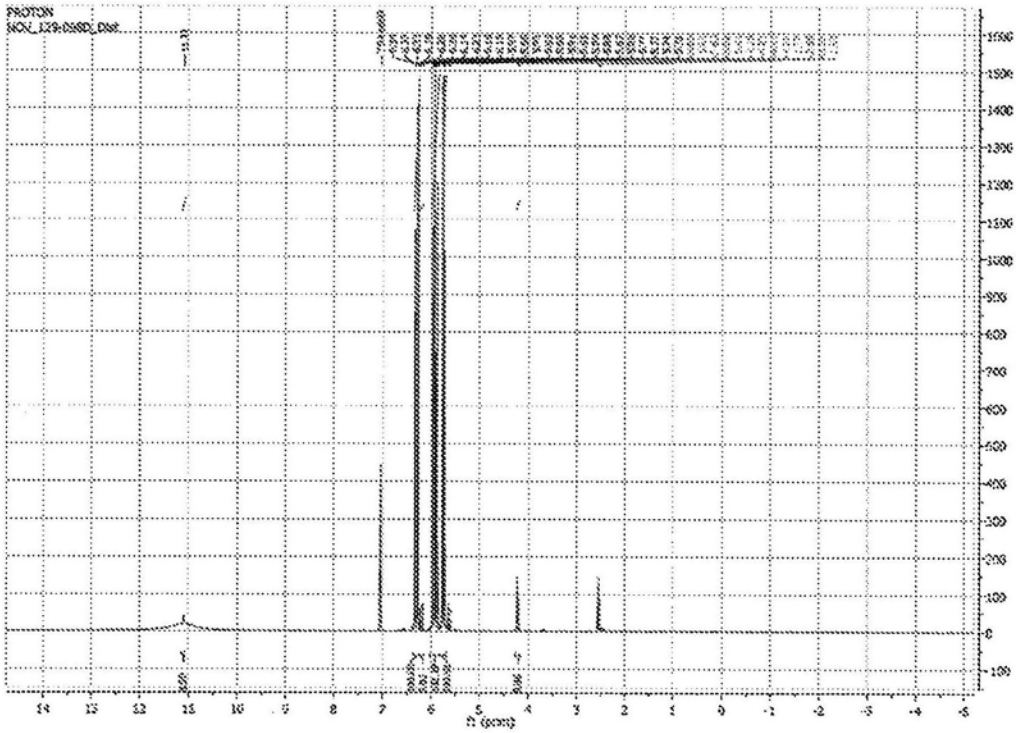


图28

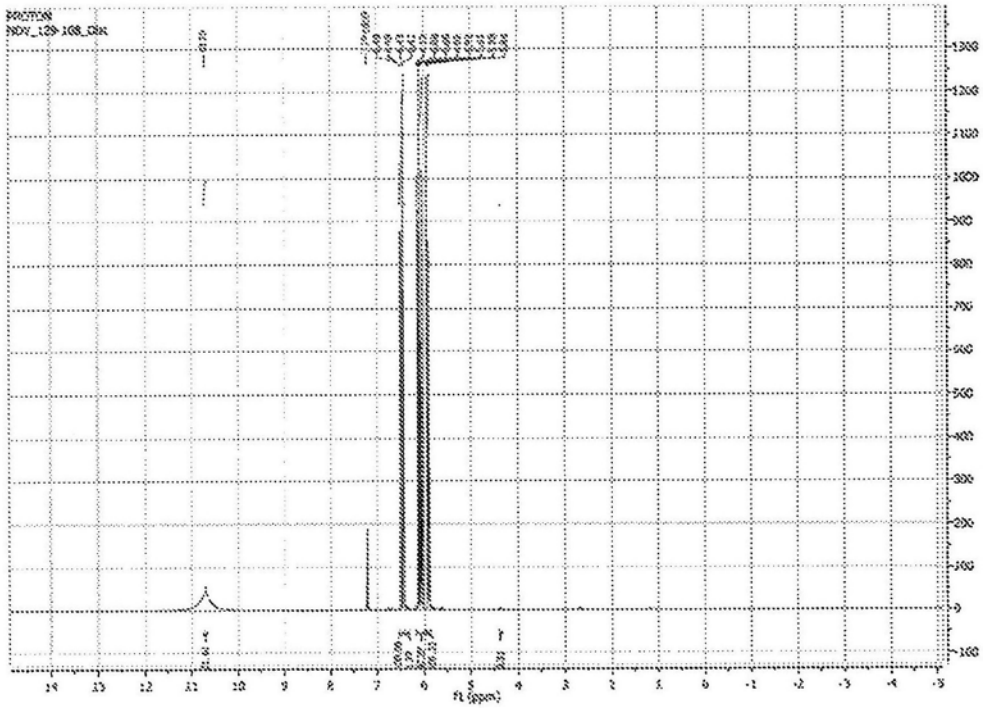


图29