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(54) Title: STABILIZING POLYPROPIOLACTONE BY END-CAPPING WITH END-CAPPING AGENTS

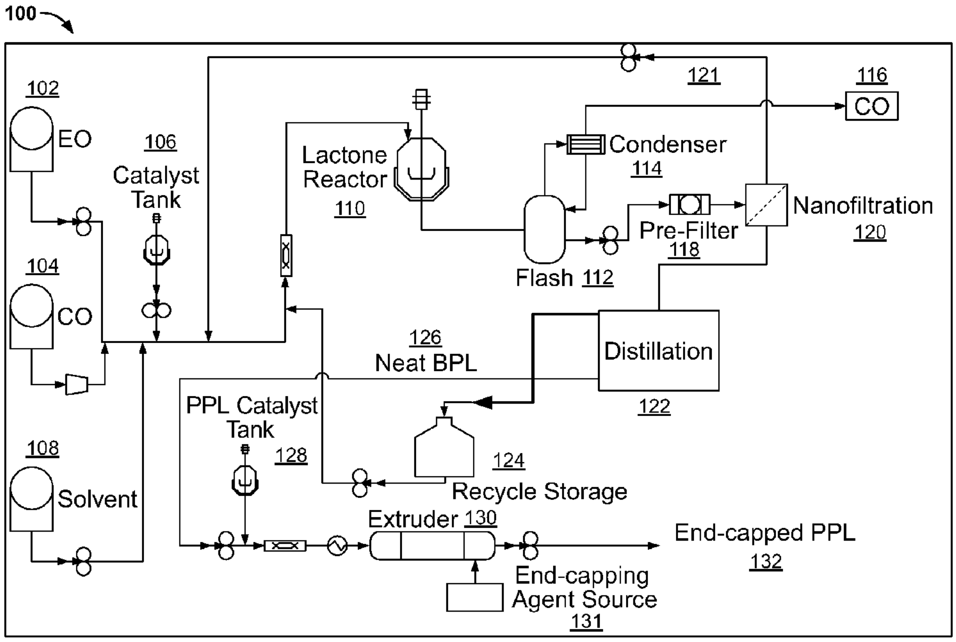

FIG. 1

(57) Abstract: Provided herein are methods and systems for producing a thermally stable polylactone polymer comprising chain terminating the polymer with an end-capping agent to prevent scission of the polymer. Also provided is a thermally stable polylactone polymer wherein the polymer has a first end and a second end, wherein at least one of said first and second ends terminate in an end-capping agent.

[Continued on next page]

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STABILIZING POLYPROPIOLACTONE BY END-CAPPING WITH END-CAPPING AGENTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application No. 62/685,205, filed June 14, 2018, which is incorporated herein by reference in its entirety.

FIELD

[0002] The present disclosure relates to more thermally stable lactone based-polyester and processes for producing more thermally stable lactone based polyesters.

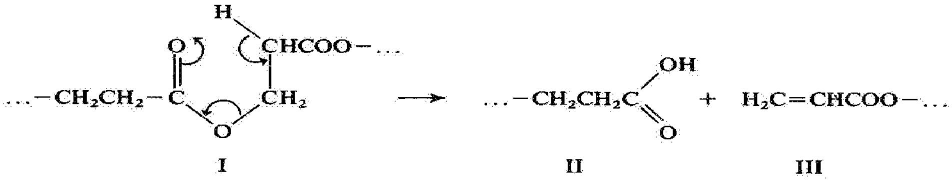
BACKGROUND

[0003] Generally, a polymer is a larger molecule comprised of multiple repeated smaller molecules called monomers. During polymerization, the monomers are covalently bonded to each other forming larger polymer chains. The composition and arrangement of the monomers determines the characteristics of the polymer. Conventional products are generally made from petroleum based polymers which may have an adverse impact on the environment.

[0004] Polypropiolactone ("PPL") is a generally biodegradable polyester polymer formed from beta lactone monomers and is useful as a material in many commercial and industrial applications. For example, low molecular weight PPL may be intentionally thermally decomposed to produce acrylic acid, a commodity chemical with many uses. In another example, high molecular weight PPL polymer is ideal for use in packaging and thermoplastic applications because of the polymer's mechanical and chemical properties. Advantageously, high molecular weight PPL may be used as an alternative to conventional petroleum based polymers, such as polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) because of PPL's advantageous barrier properties, biodegradability, and reduced environmental impact.

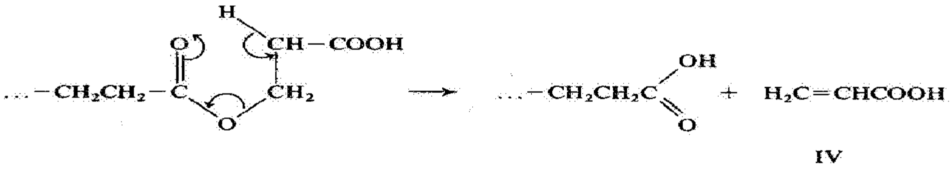
[0005] Polyester polymers suffer from increased degradation at higher temperatures. PPL may decompose at temperatures generally lower than those of conventional polyesters. The relatively low degradation temperature of PPL may be explained in terms of an ester-pyrolysis mechanism in which a cyclic transition state is involved, as depicted in Equation 1, below. This leads to two polymeric fragments, one of them (III) containing an unsaturated chain end and the other one (II) a carboxylic chain end:

Equation 1:



[0006] A polymeric fragment with the carboxylic chain end and acrylic acid (IV) may also be formed in a subsequent step (Equation 2):

Equation 2:



[0007] Thus, there exists a need for more thermally stable high molecular weight PPL.

BRIEF SUMMARY

[0008] The present invention satisfies this need by providing for end-capped PPL polymers and processes for production of end-capped PPL polymers. In some aspects, provided herein are more thermally stable PPL polymers and methods for producing the same.

[0009] In certain aspects, provided are also methods and processes for end-capping PPL with an end-capping agent to produce an end-capped PPL polymer.

[0010] In preferred embodiments, the terminal carboxylic acid functional groups of the majority of PPL polymer chains are replaced with non-carboxylic acid end groups derived from the end-capping agents. In certain preferred embodiments, the end-capping agents react with the carboxylate functional groups of the PPL to produce an end-capped PPL polymer. Advantageously, the end-capped PPL polymers are more resistant to thermal degradation.

DESCRIPTION OF THE FIGURES

[0011] 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.

[0012] FIG. 1 depicts an exemplary system for production of end-capped PPL.

[0013] FIG. 2 is a graph of isothermal viscosity curves for end-capped and non-end-capped PPL obtained at 80°C and 120 °C for 60 minutes, in accordance with features of the present invention.

[0014] FIG. 3 is a thermogravimetric analysis graph depicting the temperature at which non-end-capped PPL begins to degrade.

[0015] FIG. 4 is a thermogravimetric analysis graph depicting the temperature at which trimethylphosphate-end-capped PPL begins to degrade.

DETAILED DESCRIPTION

[0016] The following description sets forth exemplary systems, processes, 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.

[0017] All numeric values are herein assumed to be modified by the term “about”, whether or not explicitly indicated. The term “about” generally refers to a range of numbers that one of skill in the art would consider equivalent to the recited value (e.g., having the same function or result). In many instances, the terms “about” may include numbers that are rounded to the nearest significant figure.

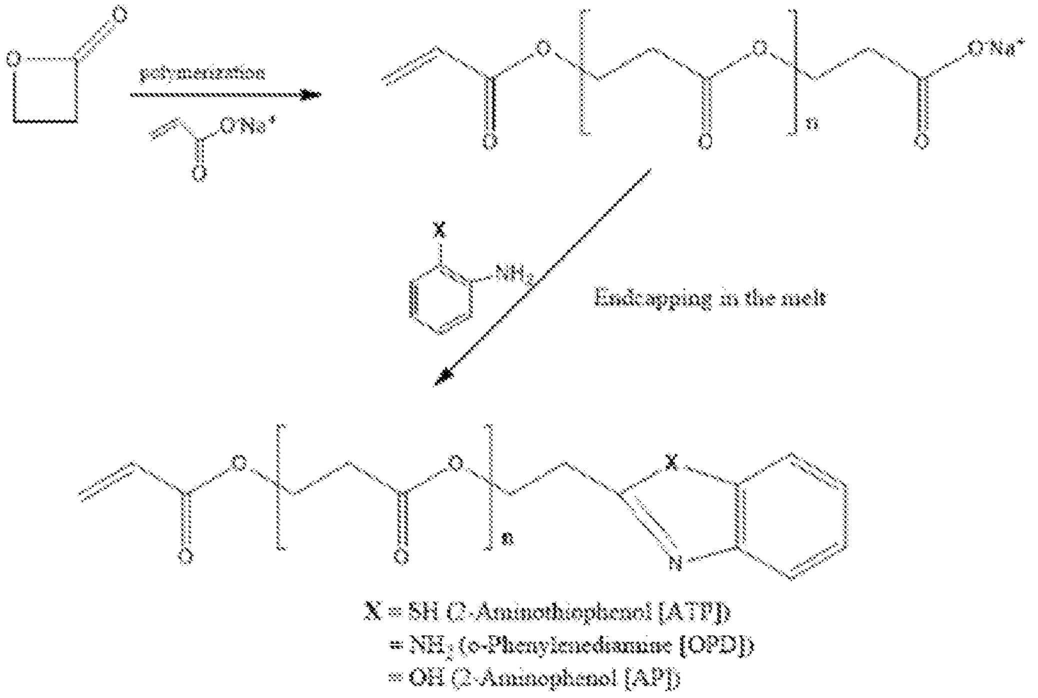
[0018] The recitation of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

[0019] As used herein, an element or step recited in the singular and preceded with the word “a” or “an” should be understood as not excluding plural said elements or steps, unless such exclusion is explicitly stated. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

[0020] Furthermore, references to "one embodiment" of the present invention are not intended to be interpreted as excluding the existence of additional embodiments that also incorporate the recited features. Moreover, unless explicitly stated to the contrary, embodiments "comprising" or "having" an element or a plurality of elements having a particular property may include additional such elements not having that property.

[0021] This invention provides methods and systems for improving the thermal stability of polylactones such as PPL. The extent to which polylactone degradation occurs depends in part on the structure of the end groups of the polymer. Polymer degradation can significantly reduce the molecular mass of the polymer, thereby changing its properties.

[0022] The figure below generally represents the reaction between polypropiolactone (PPL) and an aniline derivative end-capping agent to form end-capped PPL. The terminal carboxylic functional group of the PPL is reacted with the end-capping agent to produce a thermally stable PPL polymer.



I. Methods

[0023] In one aspect, provided are integrated processes and methods for the production of end-capped polylactones such as end-capped PPL. In certain embodiments, provided are integrated processes and methods for the production of end-capped PPL from ethylene oxide. In certain embodiments, provided are integrated processes for the conversion of ethylene oxide to end-capped PPL via carbonylation, wherein carbonylation solvent is removed following the carbonylation step and prior to PPL polymerization.

[0024] In some embodiments, provided is a method for the synthesis of end-capped PPL comprising:

polymerizing beta lactones to create PPL with a terminal carboxylic or carboxylate functional group; and

reacting the terminal carboxylic or carboxylate functional group of the PPL with an end-capping agent to produce thermally stable end-capped PPL.

[0025] Polymerization of beta lactones to PPL can be performed with a number of polymerization initiators including, for example, amines and polyamines. In some embodiments the initiator may be a nucleophile. In some embodiments the initiator may be sodium stearate, calcium stearate, and magnesium stearate. Other initiators may include sodium acrylate, sodium acetate, potassium salts of carboxylic acids in conjunction with 18-crown-6, and salts with tetramethylammonium, tetraphenylphosphonium, or 1-butyl-3-methylimidazolium cations.

[0026] Polymerization of beta lactones to PPL may further proceed in the presence of a suitable polymerization catalyst. A variety of catalysts may be used in the polymerization reaction, including, for example, metals (e.g., lithium, sodium, potassium, magnesium, calcium, zinc, aluminum, titanium, cobalt, etc.) metal oxides, carbonates of alkali- and alkaline earth metals, and borates and silicates of various metals. In some variations, catalysts that may be used in the polymerization reaction, include, for example, metals (e.g., lithium, sodium, potassium, magnesium, calcium, zinc, aluminum, titanium, cobalt, etc.) metal oxides, salts of alkali and alkaline earth metals (such as carbonates, borates, hydroxides, alkoxides, and carboxylates), and borates, silicates, or salts of other metals.

[0027] In some embodiments of provided methods, the molecular weight of the PPL may be greater than about 100,000, with improved results above about 250,000. In some embodiments, the molecular weight of the PPL is between about 100,000 and about 1,000,000, and more preferably between about 200,000 and about 400,000. In some embodiments, the molecular weight of the PPL is greater than about 350,000.

[0028] In one variation, the method further comprises pretreating the PPL by dissolving the PPL. In some embodiments, the PPL may be dissolved in chloroform. In some embodiments, the PPL may be dissolved at between about 20 °C and about 150 °C. In some embodiments the PPL may be dissolved at about 40 °C. Alternatively, the PPL may be heated to create a PPL melt.

[0029] PPL is reacted with one or more end-capping agents to produce thermally stable end-capped PPL. Suitable end-capping agents include thermally stable aniline derivatives that react with the carboxylate functional groups of the PPL. Generally, this involves a non-aqueous system. These end-capping agents decrease the extent of polymer degradation in the PPL chain.

[0030] Thermally stable aniline derivatives may include azoles such as those selected from the group consisting of benzothiazole, benzoxazole, benzimidazole, 2-aminothiophenol, o-phenylenediamine, and 2-aminophenol.

[0031] Suitable end-capping agents may further include phosphates such as those selected from the group consisting of trimethylphosphate and triphenylphosphate. Suitable end-capping agents may even further include other additives and stabilizers such as isophthalic acid.

[0032] In some embodiments, the end-capping agent may be added to the PPL at between about a 1.0 and about 2.0 mole ratio. In some embodiments, the mole ratio of end-capping agent may be about 1.5. The excess end-capping agent ensures adequate end-group access.

[0033] In some embodiments of provided methods, the PPL is reacted with the end-capping agent at a temperature of between about 0 °C and about 200 °C. In preferred embodiments, the PPL is reacted with the end-capping agent at a temperature of between about 20 and about 100 °C. In some embodiments, the PPL is reacted with the end-capping agent at about the temperature of PPL polymerization. For example, in some embodiments, the PPL is reacted with the end-capping agent at about 60 °C. Preferably, the end-capping agent is reacted with the PPL at a temperature below the decomposition temperature of the PPL. For example, the end-capping agent may be reacted with the PPL at about 25 °C.

[0034] In some embodiments of the provided methods, the PPL is reacted with the end-capping agent for between about 5 and about 30 minutes. In some embodiments, the PPL is reacted with the end-capping agent for between about 10 and about 25 minutes. In some embodiments, the PPL is reacted with the end-capping agent for about 15 minutes.

[0035] In some embodiments of the provided methods, the PPL may be reacted with the end-capping agent in a reactor. In some embodiments, the reactor may be an extruder, and the PPL may be reacted with the end-capping agent during extrusion. In some embodiments, the reactor may be a plug-flow reactor (PFR) such as a static mixer, or a continuous stirred tank reactor (CSTR), or a batch mixer.

[0036] In certain embodiments, the processes of the present invention include production of PPL from ethylene oxide as described in U.S. Application Serial No. 15/550234 filed on February 12, 2016 and herein incorporated in its entirety by reference.

[0037] In some embodiments, provided is a method for the synthesis of end-capped PPL comprising:

(a) providing feedstock streams of ethylene oxide (EO) and carbon monoxide, which feedstock streams are optionally combined;

(b) directing the feedstock streams to a first reaction zone where they are contacted with a carbonylation catalyst in the presence of a carbonylation solvent and where at least a portion of the EO is converted to a beta propiolactone (BPL) product stream comprising BPL;

(c) separating carbonylation catalyst from the beta lactone product stream to provide a carbonylation catalyst recycling stream;

(d) directing the beta propiolactone product stream comprising BPL and carbonylation solvent to a carbonylation solvent removal zone where carbonylation solvent is removed from the beta propiolactone product stream;

(e) optionally introducing a second solvent into the beta propiolactone product stream after step (d) and directing the beta propiolactone product stream to a second reaction zone where BPL is contacted with a polymerization catalyst and where at least a portion of the BPL is converted to a PPL product stream comprising PPL; and

(f) directing the PPL product stream to a third reaction zone wherein the PPL product stream is contacted with an end-capping agent and where at least a portion of the PPL is converted to end-capped PPL.

[0038] In some variations, provided is a method for the synthesis of end-capped polypropiolactone (PPL) comprising:

providing feedstock streams of ethylene oxide (EO) and carbon monoxide, wherein the feedstock streams are optionally combined;

directing the feedstock streams to a first reaction zone;

contacting the feedstock streams with a carbonylation catalyst in the presence of a carbonylation solvent in the first reaction zone to convert at least a portion of the EO to a beta propiolactone (BPL) product stream, wherein the BPL product stream comprises BPL, carbonylation catalyst, and carbonylation solvent;

separating at least a portion of carbonylation catalyst from the BPL product stream to produce a carbonylation catalyst recycling stream and a processed BPL product stream, wherein the processed BPL product stream comprises BPL and carbonylation solvent;

directing the processed BPL product stream to a carbonylation solvent removal zone;

removing at least a portion of the carbonylation solvent from the processed BPL product stream to produce a polymerization feed stream, wherein the polymerization feed stream comprises BPL;

directing the polymerization feed stream to a second reaction zone;

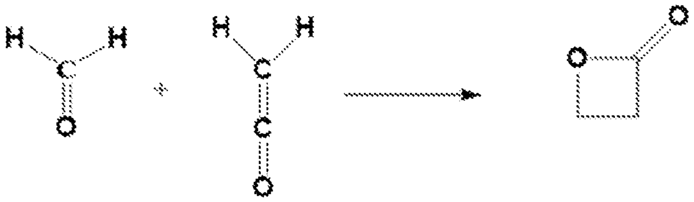
contacting BPL in the polymerization feed stream with a polymerization catalyst in the second reaction zone to convert at least a portion of the BPL to a PPL product stream;

directing the PPL product stream to a third reaction zone; and

contacting the PPL product stream with an end-capping agent in the third reaction zone to convert at least a portion of the PPL to end-capped PPL.

[0039] In some variations of the method described above, the method further comprises introducing a second solvent into the polymerization feed stream, prior to contacting the polymerization feed stream with the polymerization catalyst.

[0040] In some variations of the method described above, the BPL product stream may be formed by reacting formaldehyde with a ketene. In one variation, formaldehyde is reacted with ethenone to produce beta-propiolactone, as shown in the exemplary reaction scheme below.



[0041] In some variations of the method described above, the method may include a distillation step whereby the BPL is separated from unreacted EO, carbonylation solvent, carbonylation catalyst residue, and side products such as polyethylene oxide, acetaldehyde, and succinic anhydride.

[0042] In some embodiments of the provided methods, the third reaction zone comprises a reactor. In some embodiments, the reactor may be an extruder, and the PPL product stream may be reacted with the end-capping agent during extrusion. In other embodiments, the reactor may be a plug-flow reactor (PFR) such as a static mixer, or a continuous stirred tank reactor (CSTR), or a batch mixer.

II. Systems

[0043] In another aspect, provided are systems for the synthesis of end-capped PPL. In certain embodiments, the present invention includes a system for the production of PPL from ethylene oxide as described in U.S. Application Serial No. 15/550234 filed on February 12, 2016 and herein incorporated in its entirety by reference.

[0044] In some embodiments, a system for the conversion of ethylene oxide to end-capped polypropiolactone (PPL) comprises:

(a) ethylene oxide and carbon monoxide;

(b) a first reaction zone where ethylene oxide and carbon monoxide are contacted with a carbonylation catalyst in the presence of a carbonylation solvent, where at least a portion of the EO is converted to a beta propiolactone product stream;

(c) a solvent removal unit for removing carbonylation solvent from the beta propiolactone product stream;

(d) optionally a second solvent different from the carbonylation solvent, introduced into the beta propiolactone product stream after solvent removal;

(e) a second reaction zone where the beta propiolactone product stream is contacted with a suitable polymerization catalyst, where at least a portion of the beta propiolactone forms a PPL product stream; and

a third reaction zone where the PPL product stream is contacted with an end-capping agent, where at least a portion of the PPL forms end-capped PPL.

[0045] In some variations, provided is a system for converting ethylene oxide to PPL, comprising:

an ethylene oxide source;

a carbon monoxide source;

a carbonylation catalyst source;

a carbonylation solvent source;

a polymerization catalyst source;

a first reaction zone configured to receive ethylene oxide from the ethylene oxide source, carbon monoxide from the carbon monoxide source, carbonylation catalyst from the carbonylation catalyst source, and carbonylation solvent from the carbonylation solvent source, and to output a beta propiolactone (BPL) product stream from contacting the ethylene oxide and the carbon monoxide with the carbonylation catalyst in the presence of the carbonylation solvent in the first reaction zone, wherein the BPL product stream comprises carbonylation solvent and BPL;

a solvent removal unit configured to remove at least a portion of the carbonylation solvent from the BPL product stream;

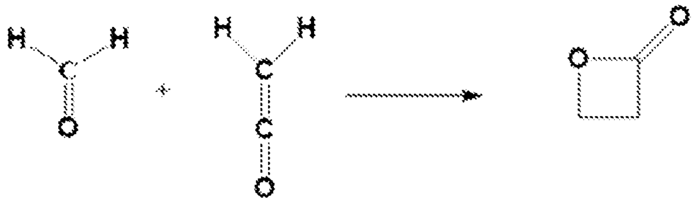
a second reaction zone configured to receive the BPL product stream from the solvent removal unit, and polymerization catalyst from the polymerization catalyst source, and to output a PPL product stream from contacting the BPL product stream with the polymerization catalyst in the second reaction zone, wherein the PPL product stream comprises PPL;

an end-capping agent source; and

a third reaction zone configured to receive the PPL product stream from the second reaction zone, and an end-capping agent from the end-capping agent source, and to output an end-capped PPL product stream from contacting the PPL product stream with the end-capping agent in the third reaction zone, wherein the end-capped PPL product stream comprises end-capped PPL.

[0046] In one variation, the system further comprises a second solvent source, wherein the second solvent source is configured to output a second solvent for combining with the BPL product stream, wherein the second solvent is different from the carbonylation solvent.

[0047] In some variations of the system described above, the BPL product stream may be formed by reacting formaldehyde with a ketene. In one variation, formaldehyde is reacted with ethenone to produce beta-propiolactone, as shown in the exemplary reaction scheme below.



[0048] In some embodiments, the third reaction zone comprises a reactor. In some embodiments, the reactor is an extruder, and the PPL product stream is reacted with the end-capping agent during extrusion. In some embodiments, the reactor may be a plug-flow reactor (PFR) such as a static mixer, or a continuous stirred tank reactor (CSTR), or a batch mixer.

[0049] It should generally be understood that reference to "a first reaction zone", "a second reaction zone", or "a third reaction zone", etc., or "a first solvent" and "a second solvent", etc., or "a first solvent source" and "a second solvent source", etc., does not necessarily imply an order of the reaction zones, solvents or solvent sources. In some variations, the use of such references denotes the number of reaction zones, solvents or solvent sources present. In other variations, an order may be implied by the context in which the reaction zones, solvents or solvent sources are configured or used.

[0050] For example, FIG. 1 depicts an exemplary system 100 for the production of end-capped PPL 132. With reference to FIG. 1, ethylene oxide (EO) from EO source 102, carbon monoxide (CO) from CO source 104, carbonylation catalyst from catalyst tank 106, and a carbonylation solvent from solvent source 108 are fed to lactone reactor 110 to produce BPL. Excess carbon monoxide 116 in the product stream exiting lactone reactor 110 may be removed via flash tank 112 and condenser 114, while the BPL product stream enters nanofiltration system 120 for removal of carbonylation catalyst. In some variations of the system, the BPL product stream may pass through pre-filter 118 prior to entry into nanofiltration unit 120. Carbonylation catalyst recycling loop 121 may feed recovered carbonylation catalyst back to lactone reactor 110. The filtered BPL product stream exiting nanofiltration unit 120 then enters distillation unit 122, wherein carbonylation solvent is removed from the BPL, and the withdrawn solvent stream may be stored in recycle storage 124 and/or returned to lactone reactor 110. PPL catalyst from PPL catalyst tank 128 is combined with neat BPL stream 126 and they collectively enter extruder reactor 130, optionally along with a second solvent (not depicted in FIG. 1). PPL synthesis occurs in extruder reactor 130. End-capping agent from end-capping agent source 131 is combined with the PPL in the extruder reactor 130 to produce end-capped PPL 132.

[0051] It should generally be understood that one or more units may be omitted or added to exemplary system 100 depicted in FIG. 1. For example, in some variations, catalyst tank 106 may be omitted in favor of using a heterogeneous carbonylation catalyst in a fixed bed arrangement in lactone reactor 110. In other variations, pre-filter 118 may be omitted, and the BPL product stream may pass through directly into nanofiltration unit 120. In other variations, carbonylation catalyst recycling loop 112 may be further purified in an additional purification unit (including, for example, an additional distillation unit) prior to return to lactone reactor 110.

[0052] It should generally be understood that any of the variations and embodiments described herein for the methods may also apply to the systems described herein.

[0053] It is to be further understood that the above description is intended to be illustrative, and not restrictive. For example, the above-described embodiments (and/or aspects thereof) may be used in combination with each other. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from its scope. While the dimensions and types of materials described herein are intended to define the parameters of the invention, they are by no means limiting, but are instead exemplary embodiments. Many other embodiments will be apparent to those of skill in the art upon reviewing the above description. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. In the appended claims, the terms “including” and “in which” are used as the plain-English equivalents of the terms “comprising” and “wherein.” Moreover, in the following claims, the terms “first,” “second,” and “third,” are used merely as labels, and are not intended to impose numerical requirements on their objects.

[0054] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," "more than" and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. In the same manner, all ratios disclosed herein also include all subratios falling within the broader ratio.

[0055] One skilled in the art will also readily recognize that where members are grouped together in a common manner, such as in a Markush group, the present invention encompasses not only the entire group listed as a whole, but each member of the group individually and all possible subgroups of the main group. Accordingly, for all purposes, the present invention encompasses not only the main group, but also the main group absent one or more of the group members. The present invention also envisages the explicit exclusion of one or more of any of the group members in the claimed invention.

EXAMPLES

[0056] The following examples are merely illustrative and are not meant to limit any aspects of the present disclosure in any way.

Example 1

[0057] A high molecular weight (e.g., MW >450,000) PPL was dissolved in solvent (e.g., chloroform) at 40 °C. A 3 weight percent solution was prepared in two separate jars by dissolving 3.76 g PPL in 121.59 g $CHCl_3$ and 4.57g PPL in 147.76 g $CHCl_3$, respectively. In three separate vials, 40 g of the PPL solution (i.e. 1.2 g neat polymer basis) was taken and 1.5 mole ratio end-capping agents was dissolved in the PPL solution at room temperature. The solvent was subsequently removed by evaporation under vacuum before being heated to 80 °C. The 50 percent excess end-capping agent was chosen to ensure adequate end-group access.

Example 2

[0058] 0.00075 mg of 2-aminothiophenol was added to 1.2 g of 450,000 MW PPL and heated to 80 °C for 45 minutes–as described in Example 1. The diffusion NMR results showed that non-capped PPL had a molecular weight of 220,000 after heating while the 2-aminothiophenol end-capped PPL had a molecular weight of 450,000.

Example 3

[0059] 0.0005 mg of o-phenylenediamine was added to 1.2 g of 450,000 MW PPL and heated to 80 °C for 45 minutes—as described in Example 1. The diffusion NMR results showed that non-capped PPL had a molecular weight of 220,000 after heating while the o-phenylenediamine end-capped PPL had a molecular weight of 450,000.

[0060] Tables 1 and 2 display stability tests for the ATP- and OPD-capped polymers at 72 °C and 120 °C, respectively.

Table 1: Hydrolytic Stability tests in water at 72 °C

Polymer	MW after stirring in hot water for 1 hour at 72 °C
Control PPL	180,000
ATP-PPL	364,000
OPD-PPL	382,000

Table 2: Molecular weights of the polymers after heating for 1 hour at 120 °C

Polymer	MW after heating for 1 hour at 120 °C
ATP-PPL	362,000
OPD-PPL	323,000

[0061] These results show a much higher molecular weight of the end-capped polymer versus uncapped polymer after heat testing. The data show that the aniline-capped PPL does not degrade as easily as the non-capped PPL.

[0062] FIG. 2 is a graph of the dynamic viscosity values of ATP-end-capped PPL over a temperature range from about 80 °C to about 120 °C. FIG. 2 demonstrates that ATP-end-capped PPL degrades to a lesser extent than non-end-capped PPL at high temperatures. Specifically, FIG. 2 shows that ATP-end-capped PPL maintains higher viscosities than non-end-capped PPL after being heated to about 80 °C and about 120 °C.

[0063] The above description covers end-capping of a sodium-free high molecular weight PPL. More experiments were done using PPL made with a sodium stearate initiator and end-capped with aminothiophenol. The experiment was performed in the same manner as described above with a 180,000 – 190,000 MW PPL made using a sodium stearate initiator. A summary of the results is shown in Table 3 below.

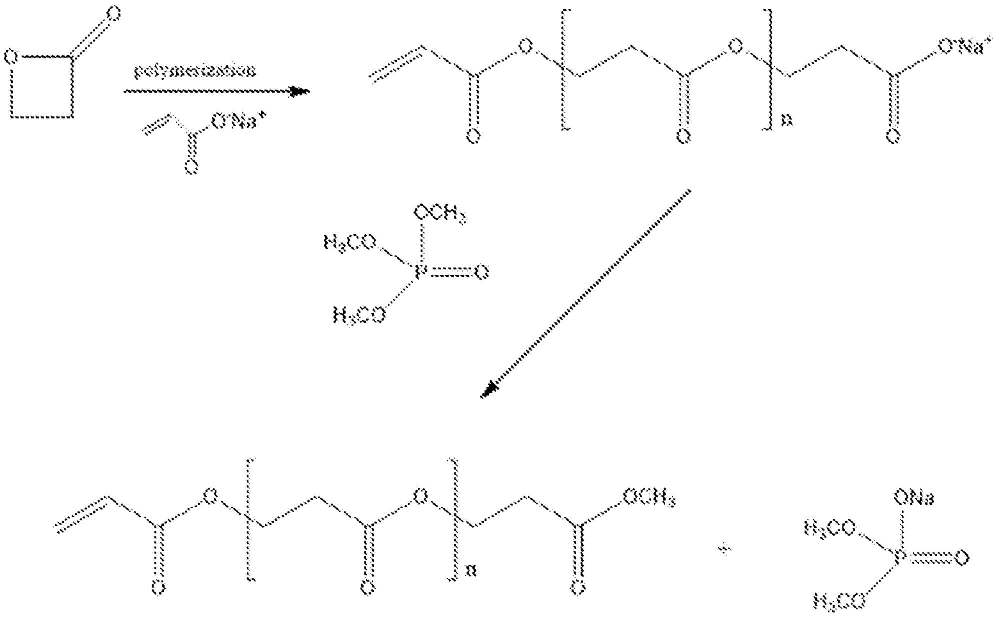
Table 3: Aminothiophenol end-capped PPL at 40 °C, 80 °C and 120 °C heat treatment

Sample ID	Initial state (from $CHCl_3$ at 25 °C)	T = 40 °C (overnight stirring in bath)	T = 80 °C (heated for 45 mins at temp)	T = 120 °C (heated for 30 minutes at temp)
Control PPL	180,000	166,000	137,000	69,000
ATP-PPL	180,000	171,000	133,000	102,000

[0064] Table 3 illustrates the difference in molecular weight between ATP-end-capped PPL and non-end-capped PPL after being heated. The initial molecular weights of PPL were between about 180,000 and 190,000. It was observed that ATP-end-capped PPL had a higher molecular weight than control PPL after being heated to 40 °C overnight and after being heated to 120 °C for 30 minutes. These results demonstrate that at high temperatures (T = 120 °C), ATP-end-capped PPL degrades to a much lesser extent than non-end-capped PPL. The ordinate units of the graph is poise (P) and the abscissa is in seconds.

Example 4

[0065] 20 mL of a roughly 10 wt% chloroform solution of PPL was treated with five drops of neat trimethylphosphate. The mixture was stirred overnight. The PPL was then precipitated in 50 mL of isopropanol. The reaction between the PPL and the trimethylphosphate is illustrated in the figure below.



[0066] FIG. 3 is a TGA graph showing the onset of degradation temperature for the non-end-capped PPL (205.78°C). FIG. 4 is a TGA graph showing the onset of degradation temperature for the trimethylphosphate-end-capped PPL (225.51°C). The temperature of degradation onset was 20 °C higher for trimethylphosphate-end-capped PPL than the non-end-capped PPL. These results demonstrate the increased thermostability of end-capped PPL.

CLAIMS

What is claimed is:

1. A thermally-stable polylactone polymer, wherein the polymer has a first end and a second end, and wherein at least one of said ends terminates in an end-capping agent.

2. The polymer of claim 1, wherein the end-capping agent is an azole.

3. The polymer of claim 2, wherein the azole is benzothiazole, benzoxazole, benzimidazole, 2-aminothiophenol, o-phenylenediamine, or 2-aminophenol, or any combinations thereof.

4. The polymer of claim 1, wherein the end-capping agent is trimethylphosphate.

5. The polymer of claim 1, wherein the end-capping agent is triphenylphosphate.

6. The polymer of any one of claims 1 to 5, wherein the polymer has a molecular weight of between about 100,000 and about 1,000,000 at a temperature between about 0°C and about 100°C.

7. The polymer of any one of claims 1 to 5, wherein the polymer has a molecular weight of between about 200,000 and about 400,000 at a temperature between about 0°C and about 100°C.

8. The polymer of any one of claims 1 to 7, wherein the polymer is stable in both aqueous and non-aqueous systems.

9. A method for producing a thermally stable polylactone polymer, comprising chain terminating a polylactone polymer with an end-capping agent to prevent scission of the polymer.

10. The method of claim 9, wherein the end-capping agent is an azole.

11. The method of claim 10, wherein the azole is benzothiazole, benzoxazole, benzimidazole, 2-aminothiophenol, o-phenylenediamine, or 2-aminophenol, or any combinations thereof.

12. The method of claim 9, wherein the end-capping agent is trimethylephosphate.

13. The method of claim 9, wherein the end-capping agent is triphenylephosphate.

14. The method of any one of claims 9 to 13, wherein the end-capping agent reacts with the polymer during polymer formation.

15. The method of any one of claims 9 to 13, wherein the end-capping agent reacts with the already formed polymer.

16. The method of any one of claims 9 to 15, wherein chain termination occurs at room temperature.

17. A method for producing end-capped polypropiolactone (PPL), comprising:

providing feedstock streams of ethylene oxide (EO) and carbon monoxide, wherein the feedstock streams are optionally combined;

directing the feedstock streams to a first reaction zone;

contacting the feedstock streams with a carbonylation catalyst in the presence of a carbonylation solvent in the first reaction zone to convert at least a portion of the EO to a beta propiolactone (BPL) product stream, wherein the BPL product stream comprises BPL, carbonylation catalyst, and carbonylation solvent;

separating at least a portion of carbonylation catalyst from the BPL product stream to produce a carbonylation catalyst recycling stream and a processed BPL product stream, wherein the processed BPL product stream comprises BPL and carbonylation solvent;

directing the processed BPL product stream to a carbonylation solvent removal zone;

removing at least a portion of the carbonylation solvent from the processed BPL product stream to produce a polymerization feed stream, wherein the polymerization feed stream comprises BPL;

directing the polymerization feed stream to a second reaction zone;

contacting BPL in the polymerization feed stream with a polymerization catalyst in the second reaction zone to convert at least a portion of the BPL to a PPL product stream;

directing the PPL product stream to a third reaction zone; and

contacting the PPL product stream with an end-capping agent in the third reaction zone to convert at least a portion of the PPL to end-capped PPL.

18. The method of claim 17, further comprising introducing a second solvent into the polymerization feed stream, prior to contacting the polymerization feed stream with the polymerization catalyst.

19. The method of claim 17, wherein the third reaction zone is an extruder.

20. A system for converting ethylene oxide to end-capped polypropiolactone (PPL), comprising:

an ethylene oxide source;

a carbon monoxide source;

a carbonylation catalyst source;

a carbonylation solvent source;

a polymerization catalyst source;

a first reaction zone configured to receive ethylene oxide from the ethylene oxide source, carbon monoxide from the carbon monoxide source, carbonylation catalyst from the carbonylation catalyst source, and carbonylation solvent from the carbonylation solvent source, and to output a beta propiolactone (BPL) product stream from contacting the ethylene oxide and the carbon monoxide with the carbonylation catalyst in the presence of the carbonylation solvent in the first reaction zone, wherein the BPL product stream comprises carbonylation solvent and BPL;

a solvent removal unit configured to remove at least a portion of the carbonylation solvent from the BPL product stream;

a second reaction zone configured to receive the BPL product stream from the solvent removal unit, and polymerization catalyst from the polymerization catalyst source, and to output a PPL product stream from contacting the BPL product stream with the polymerization catalyst in the second reaction zone, wherein the PPL product stream comprises PPL;

an end-capping agent source; and

a third reaction zone configured to receive the PPL product stream from the second reaction zone, and an end-capping agent from the end-capping agent source, and to output an end-capped PPL product stream from contacting the PPL product stream with the end-capping agent in the third reaction zone, wherein the end-capped PPL product stream comprises end-capped PPL.

21. The system of claim 20, further comprising a second solvent source, wherein the second solvent source is configured to output a second solvent for combining with the BPL product stream, wherein the second solvent is different from the carbonylation solvent.

22. The system of claim 20, wherein the third reaction zone is an extruder.

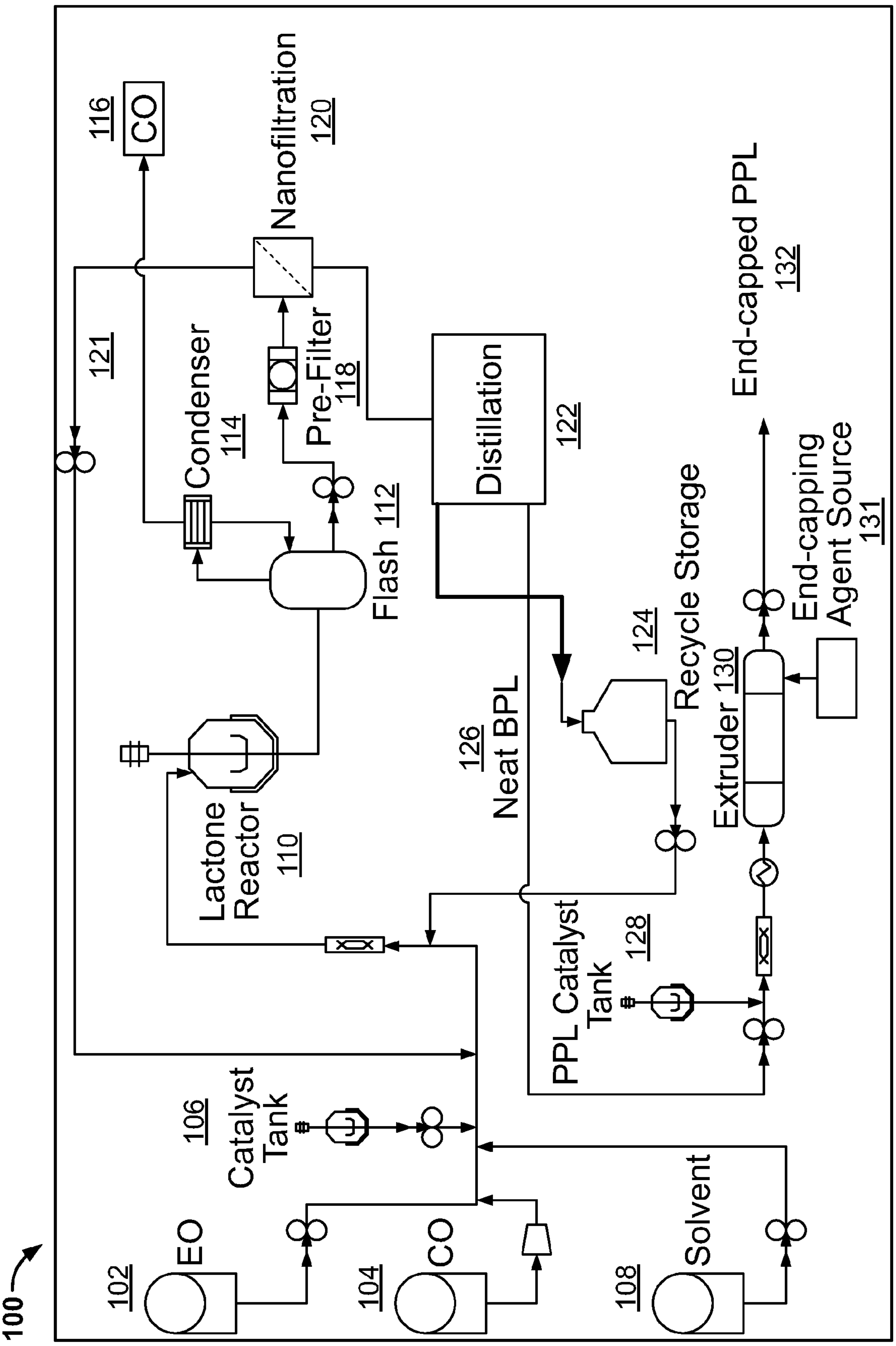

100
102
EO
104
CO
108
Solvent
106
Catalyst Tank
Lactone Reactor
110
116
CO
121
Condenser
114
Flash 112
Pre-Filter
118
Nanofiltration
120
Distillation
122
126
Neat BPL
124
Recycle Storage
PPL Catalyst Tank
128
Extruder 130
End-capping Agent Source
131
End-capped PPL
132

FIG. 1

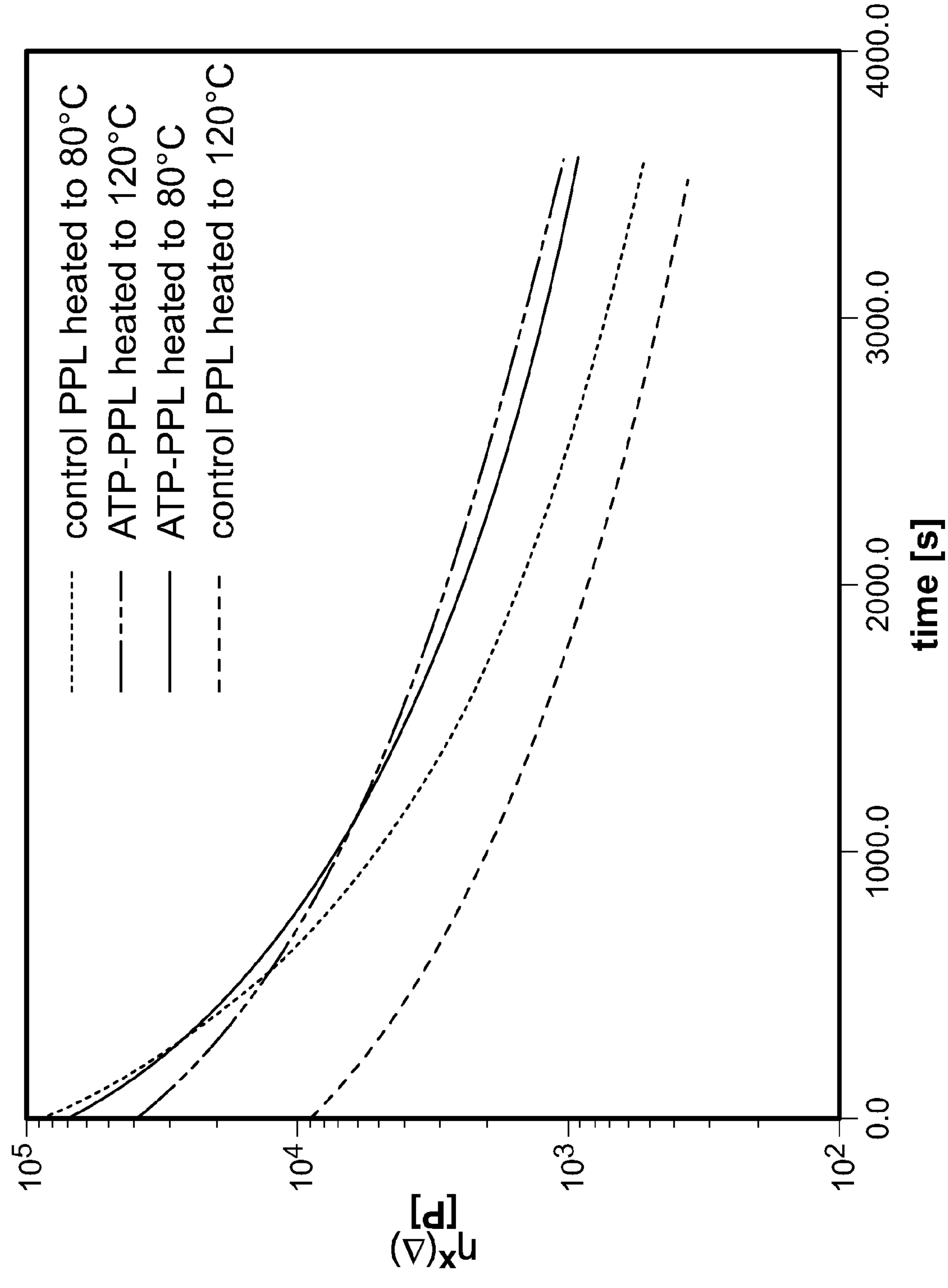

control PPL heated to 80°C
ATP-PPL heated to 120°C
ATP-PPL heated to 80°C
control PPL heated to 120°C
$\eta^{x}(\Delta)$
[P]
10^5
10^4
10^3
10^2
0.0
1000.0
2000.0
3000.0
4000.0
time [s]

FIG. 2

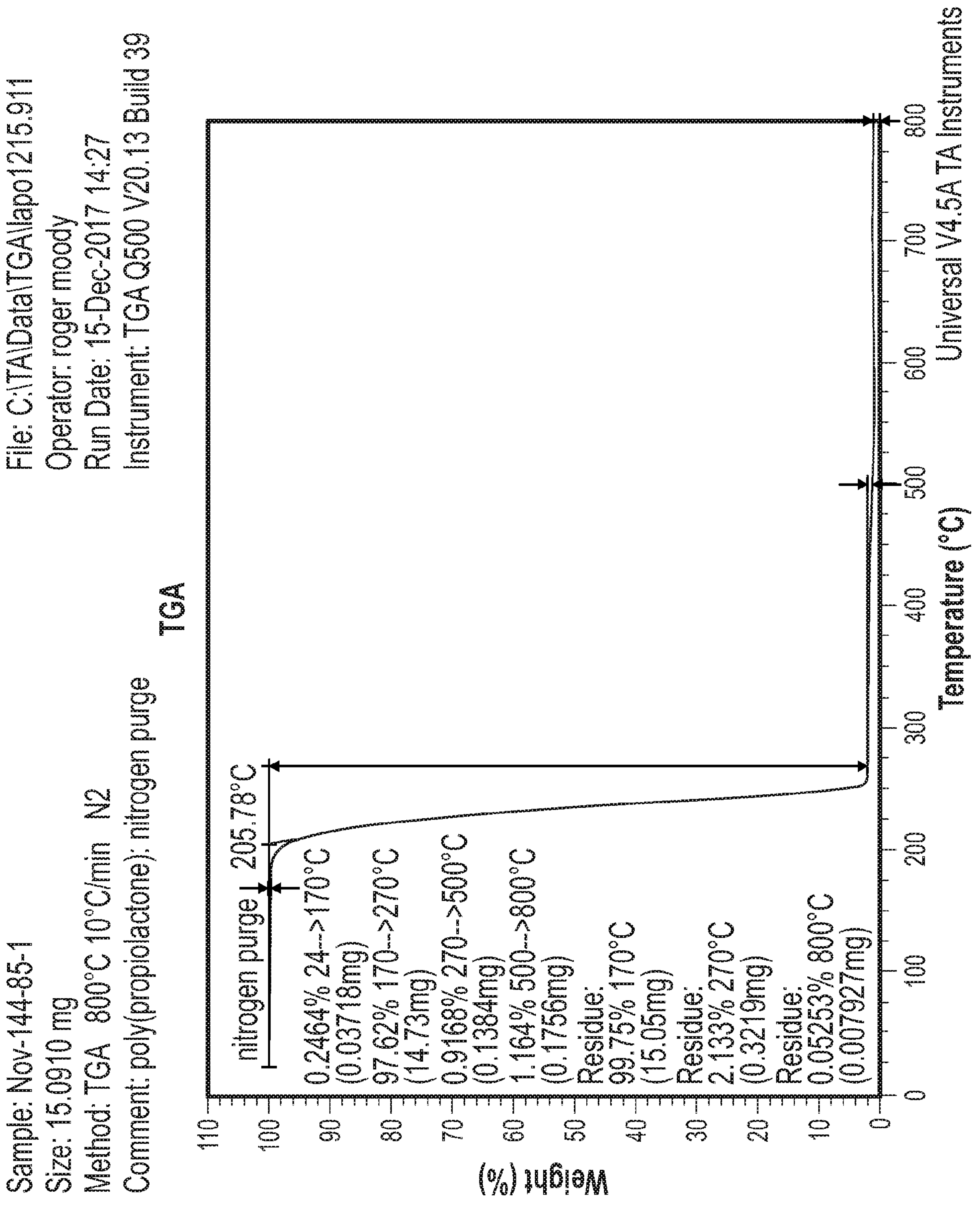

Sample: Nov-144-85-1
Size: 15.0910 mg
Method: TGA 800°C 10°C/min N2
Comment: poly(propiolactone): nitrogen purge
TGA
File: C:\TA\Data\TGA\apo1215.911
Operator: roger moody
Run Date: 15-Dec-2017 14:27
Instrument: TGA Q500 V20.13 Build 39
nitrogen purge
205.78°C
0.2464% 24-->170°C
(0.03718mg)
97.62% 170-->270°C
(14.73mg)
0.9168% 270-->500°C
(0.1384mg)
1.164% 500-->800°C
(0.1756mg)
Residue:
99.75% 170°C
(15.05mg)
Residue:
2.133% 270°C
(0.3219mg)
Residue:
0.05253% 800°C
(0.007927mg)
Weight (%)
110
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
Temperature (°C)
Universal V4.5A TA Instruments

FIG. 3

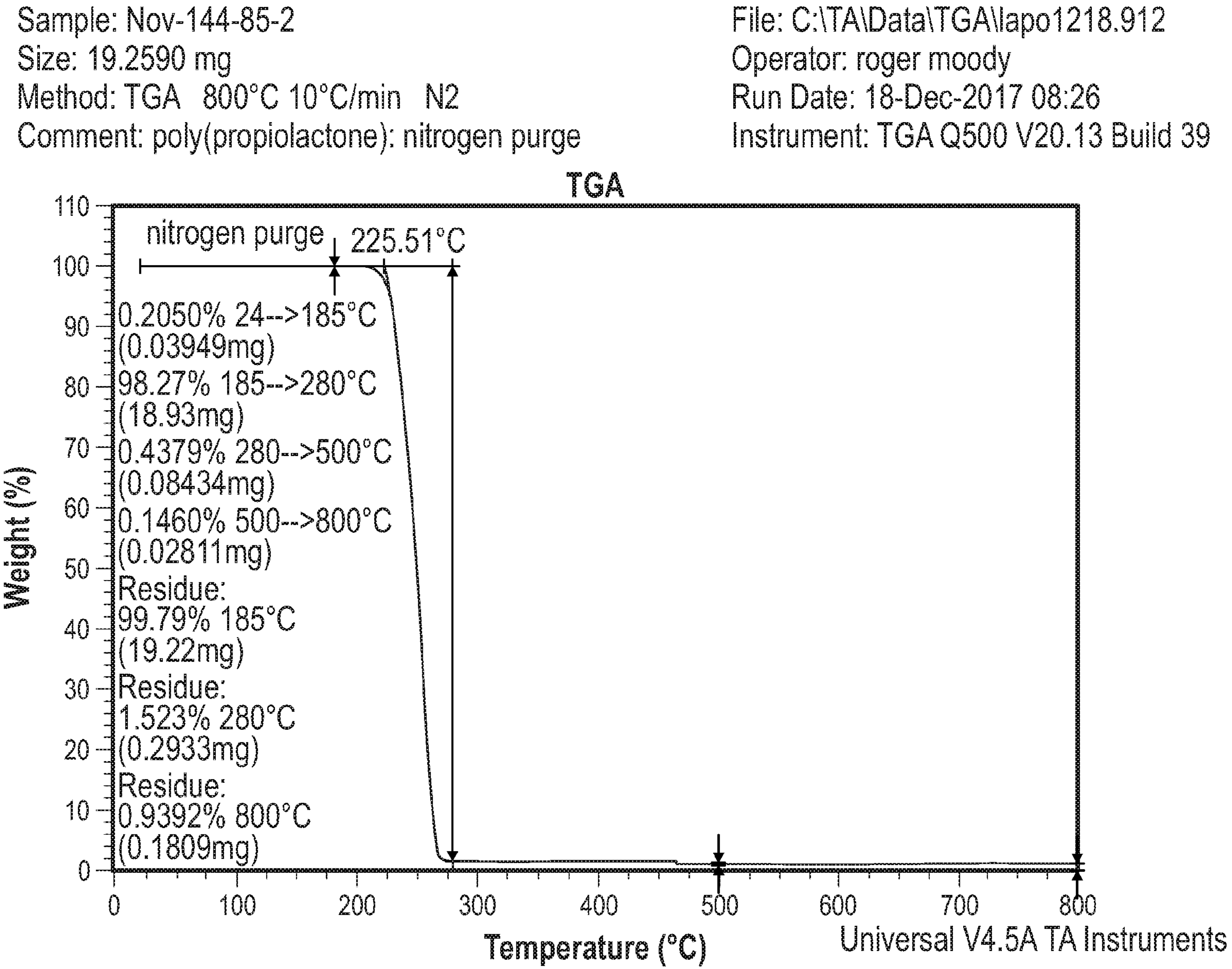

Sample: Nov-144-85-2
Size: 19.2590 mg
Method: TGA 800°C 10°C/min N2
Comment: poly(propiolactone): nitrogen purge
File: C:\TA\Data\TGA\lapo1218.912
Operator: roger moody
Run Date: 18-Dec-2017 08:26
Instrument: TGA Q500 V20.13 Build 39
TGA
nitrogen purge
225.51°C
0.2050% 24-->185°C
(0.03949mg)
98.27% 185-->280°C
(18.93mg)
0.4379% 280-->500°C
(0.08434mg)
0.1460% 500-->800°C
(0.02811mg)
Residue:
99.79% 185°C
(19.22mg)
Residue:
1.523% 280°C
(0.2933mg)
Residue:
0.9392% 800°C
(0.1809mg)
Weight (%)
110
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
Temperature (°C)
Universal V4.5A TA Instruments

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/37103

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08L 67/02 (2019.01)
CPC - C08K 5/0066; C08K 5/34924; C08K 5/521; C08K 5/5313; C08K 5/5399

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)
See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2018/0094100 A1 (Novomer, Inc.) 5 April 2018 (05.04.2018) Entire document, especially Abstract, para [0002], [0020], [0059], [0262]	1, 6/1, 7/1 --- 2-5, (6-7)/(2-5)
Y	Uittenbogaard et al. "Reactions of Beta-Propiolactone with Nucleobase Analogues, Nucleosides, and Peptides." Journal of Biological Chemistry, vol. 286, no. 42, 2011, pp. 36198-36214., doi:10.1074/jbc.m111.279232. Entire document, especially pages 1, 8-11; Table 2	2-3, 6/(2-3), 7/(2-3)
Y	US 4,536,531 A (Ogawa et al.) 20 August 1985 (20.08.1985) Entire document, especially Abstract, col 14 ln 6-8; col 22 ln 22-26; col 23 ln 14-22; col 24 ln 34-62; Table 3	4-5, 6/(4-5), 7/(4-5)
A	US 3,835,089 A (Fox et al.) 10 September 1974 (10.09.1974) Entire document	1-7
A	US 4,963,595 A (Ward et al.) 16 October 1990 (16.10.1990) Entire document	1-7
A, P	US 10,221,278 B2 (Novomer, Inc.) 5 March 2019 (05.03.2019) Entire document	1-7
A, P	US 10,221,150 B2 (Novomer, Inc.) 5 March 2019 (05.03.2019) Entire document	1-7

☐ 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 19 August 2019	Date of mailing of the international search report 22 OCT 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/37103

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.:
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:

3. ☒ Claims Nos.: 8, 16
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:

-- See Extra Sheets --

1. ☐ As all required additional 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 additional fees, this Authority did not invite payment of 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.:
1-7

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.

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-7, directed to a thermally-stable polylactone polymer, wherein the polymer has a first end and a second end, and wherein at least one of said ends terminates in an end-capping agent.

Group II: Claims 9-15 and 17-22, directed to a method for producing a thermally stable polylactone polymer, comprising chain terminating a polylactone polymer with an end-capping agent.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group II requires a method for producing a thermally stable polylactone polymer, comprising chain terminating a polylactone polymer with an end-capping agent, not required by Group I.

Common Technical Features:

Groups I-II share the technical features of a thermally-stable polylactone polymer, wherein the polymer has a first end and a second end, and wherein at least one of said ends terminates in an end-capping agent.

However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by US 2018/0094100 A1 to Novomer, Inc. Novomer disclose a thermally-stable polylactone polymer (para [0002] - '... The present disclosure relates generally to poly propiolactone and methods of producing thereof...'; para [0262] - '... In some embodiments, the reaction zone is maintained at a temperature suitable for the formation of poly propiolactone polymers...'; para [0059] - '... Combinations of substituents envisioned herein are prefer ably 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 certain embodiments, their recovery, purification...'), wherein the polymer has a first end and a second end (para [0020] - '... a polymer chain comprising repeating units having the structure...'; see Figure within para [0020]), and wherein at least one of said ends terminates in an end-capping agent (para [0020] - '... wherein the acrylate end group or the hydracrylate end group caps the alkyl terminus of the polymer chain...').

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I and II lack unity under PCT Rule 13.