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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 May 2025 (22.05.2025)

WIPO | PCT

(10) International Publication Number
WO 2025/106936 A1

(51) International Patent Classification:
C08F 22/02 (2006.01) *C08F 220/06* (2006.01)
C08F 220/04 (2006.01)

(21) International Application Number: PCT/US2024/056301

(22) International Filing Date: 15 November 2024 (15.11.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/600,004 16 November 2023 (16.11.2023) US

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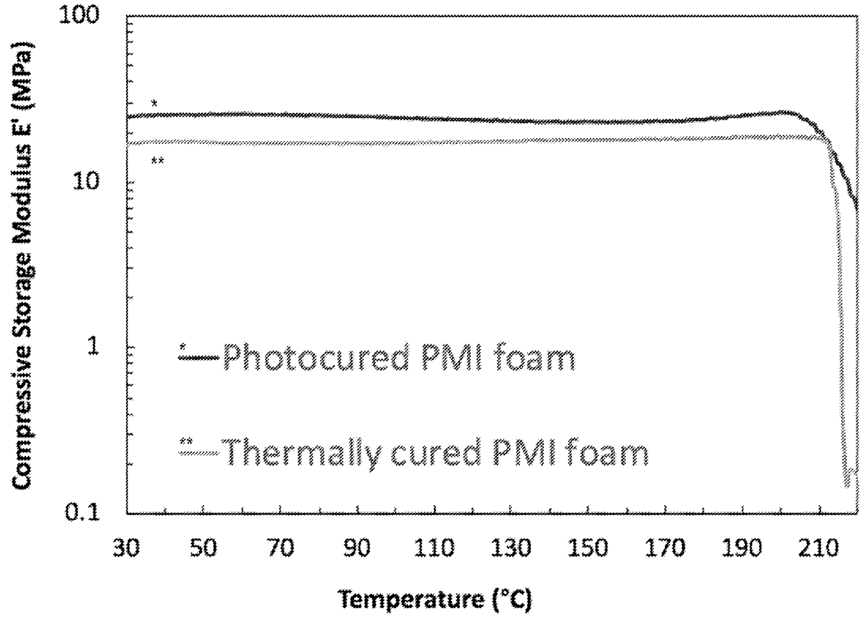
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,

(54) Title: POLY(METH)ACRYLIMIDE MATERIALS WITH ENHANCED THERMOMECHANICAL PROPERTIES

FIG. 1



(57) Abstract: The disclosure relates to a method for producing poly(meth)acrylimides by the copolymerization of (meth)acrylates, (meth)acrylamides and/or (meth)acrylonitrile under the influence of actinic radiation. The resulting precursor polymer resin may be imidized and/or foamed by thermal treatment.

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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))*

POLY(METH)ACRYLIMIDE MATERIALS WITH ENHANCED THERMOMECHANICAL PROPERTIES

RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Application No. 63/600,004, filed November 16, 2023, and entitled "Poly(methacrylimide) Materials with Enhanced Thermomechanical Properties," which is herein incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] This disclosure relates to the formation of poly(meth)acrylimides, *e.g.*, polymethacrylimides and polyacrylimides, in some instances having defined geometry, by copolymerization of monomers under the influence of actinic radiation. Subsequent to polymerization, thermal treatment may be employed to form a poly(meth)acrylimide.

BACKGROUND

[0003] It is known how to produce poly(meth)acrylimide foams in the form of blocks. The first step is to copolymerise (meth)acrylic acid and (meth)acrylonitrile with each other to form a precursor copolymer that already has a corresponding sheet form. The copolymer is then thermally cyclised to form the imide. A blowing agent in the reaction mixture ensures that the corresponding foam is formed on heating.

[0004] Existing processes largely rely on thermally initiated bulk free-radical polymerizations to form the precursor polymer, which are energy intensive and often require long reaction periods (*e.g.*, hours to days), oxygen-free environments, and precise temperature control.

[0005] However, existing processes have the disadvantage that either large amounts of residual monomer remain in the product during or after synthesis, or a great deal of effort, expense and inconvenience must be invested to reduce the residual monomer content. For example, existing processes often require additional post-processing steps to reduce the monomer content. The residual monomer content is particularly concerning when the toxic (meth)acrylonitrile, *e.g.*, methacrylonitrile or acrylonitrile, is used. This toxicity limits the utility of existing processes in applications that require human workers to manipulate intermediates or products comprising (meth)acrylonitrile.

[0006] It is further a frequent issue with existing processes to produce polymer sheets up to 30 mm or above in thickness directly. To achieve a safe and uniform polymerisation process, the polymerisation system has to be alternatingly cooled and heated, particularly because overheating means that the polymerisation is no longer controllable and non-uniform structures are formed. These alternating cooling and heating phases are inconvenient and have limitations, such as high energy, water, and time requirements. Existing processes are also not readily adaptable to afford complex shapes of the poly(meth)acrylimide.

[0007] The inefficiency and toxicological concerns of existing processes contribute to the limited commercial availability of poly(meth)acrylimide materials. Accordingly, alternative methods to generate poly(meth)acrylimides are desirable.

SUMMARY OF THE DISCLOSURE

[0008] Provided herein are improved methods of preparing poly(meth)acrylimide materials and associated precursor polymers. Some embodiments relate to the synthesis of poly(meth)acrylimide (P(M)I) materials and associated precursor polymer, which are optionally foamed, which may have low residual monomer contents, and/or which may have a toxicologically unconcerning utility. Some embodiments relate to a process for producing such P(M)I materials and associated precursor polymer which are optionally foamed in a relatively efficient (*e.g.*, short time) and/or advantageous manner from the perspectives of one or more of time, cost, processing condition including but not restricted to temperature and pressures, the number of processing steps and/or geometry.

[0009] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation to form a solid layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer; and

(b) imidizing the precursor polymer to generate the poly(meth)acrylimide.

[0010] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation to form a solid layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

(b) imidizing at least a section of the solid layer of the precursor polymer to generate the poly(meth)acrylimide.

[0011] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation to form a layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

at the end of the irradiation, the reaction mixture has a percent conversion of at least 40%; and

(b) imidizing at least a section of the layer of the precursor polymer to generate the poly(meth)acrylimide.

[0012] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

at the start of the irradiation, a percent conversion of the reaction mixture is less than 10%;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500nm and/or comprises electron beam radiation; and

at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 20%; and

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

[0013] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

[0014] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation comprising actinic radiation to form a precursor polymer, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules, a near-infrared dye, and an initiator,

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer, and

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 2500nm; and

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

[0015] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising:

irradiating a material comprising a precursor polymer and a near-infrared dye with radiation comprising actinic radiation to imidize at least a portion of the precursor polymer to generate the poly(meth)acrylimide,

wherein:

the precursor polymer comprises an optionally substituted polyacrylate, an optionally substituted polyacrylamide, an optionally substituted polyacrylonitrile, an optionally substituted polyacrylic acid, and/or any copolymer thereof, and

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 2500.

[0016] In some embodiments, provided herein is a poly(meth)acrylimide prepared according to any method provided herein.

[0017] In some embodiments, a process for producing poly(meth)acrylimide resins described herein proceeds by copolymerization of a (meth)acrylic acid or (meth)acrylic ester, or combination thereof, with a (meth)acrylamide or (meth)acrylonitrile, or combination thereof, with or without further copolymerizable comonomers. Such a process may comprise the two or three process steps of polymerization, imidization, and, optionally, foaming. In some embodiments, the process for producing poly(meth)acrylimide resins optionally capable of forming foams proceeds by copolymerization of a (meth)acrylic acid or (meth)acrylic ester, or combination thereof, with (meth)acrylamides or (meth)acrylonitrile, or combination thereof, with or without further copolymerizable comonomers in the three process steps of polymerization in the presence of free-radical initiators activated by actinic radiation, imidization and optionally foaming.

[0018] In some embodiments, the methods provided herein can be employed to generate poly(meth)acrylimide materials (*e.g.*, resins and/or foams comprising a poly(meth)acrylimide). In some embodiments, the methods provided herein generate a poly(meth)acrylimide resin that may be capable of being foamed and/or may optionally undergo foaming.

[0019] The resulting P(M)I foams may be of high quality, particularly with regard to the geometry obtainable and/or thermomechanical properties, and/or may have a uniform distribution of closed cells.

[0020] In some embodiments, this disclosure provides uniform PMI materials in the form of arbitrary geometries by employing photoinitiated polymerizations. This approach provided herein can allow greater control and/or reliability of the polymerization process, sometimes with overall reduced energy consumption and/or processing time, typically in the order of hours.

[0021] In some embodiments, toxic optionally substituted acrylonitrile (*e.g.*, (meth)acrylonitrile) is avoided as monomer for the production of PMI, without negatively impacting the thermomechanical properties of the PMI materials obtained, or instead improving them. In some embodiments, the present disclosure provides a process whereby a poly(meth)acrylimide is obtained without the use of an optionally substituted acrylonitrile monomer. In some embodiments, the present disclosure provides a process whereby poly(meth)acrylimide foams are obtainable without the use of an optionally substituted acrylonitrile monomer. In some embodiments, the present disclosure provides a process whereby poly(meth)acrylimide foams (P(M)I foams) are obtainable without the use of (meth)acrylonitrile. This object can be achieved by a method for producing optionally foamable polymethacrylimide materials by copolymerization of methacrylic acid/esters and methacrylamides, as well as optionally further copolymerizable monomers in the presence of radical-forming initiators, thermally induced imidization of the copolymer to poly(meth)acrylimide, and optional transformation to a foamed material, which can be characterized in that the copolymerization is performed photochemically by optionally using additive manufacturing techniques.

[0022] The details of certain embodiments of the invention are set forth in the Detailed Description of Certain Embodiments, as described below. Other features, objects, and advantages of the invention will be apparent from the Definitions, Examples, Figures, and Claims. It should be understood that the aspects and embodiments described herein are not limited to specific embodiments, methods, or configurations, and as such can, of course, vary.

It is also to be understood that the terminology used herein is for the purpose of describing particular aspects and embodiments only and, unless specifically defined herein, is not intended to be limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] The accompanying drawings, which constitute a part of this specification, illustrate several embodiments of the present disclosure and together with the description, provide non-limiting examples of the disclosure. The figures are exemplary and do not limit the scope of the present disclosure. The accompanying drawings are not drawn to scale. In the drawings, each identical or nearly identical component that is illustrated in the various figures is represented by a like numeral. For purposes of clarity, not every component may be labeled in every drawing. In the drawings:

[0024] FIG. 1 illustrates a dynamic mechanical analysis (DMA) plot of compressive modulus as a function of temperature for PMI foam materials produced using thermal curing and photocuring; and

[0025] FIG 2 illustrates a dynamic mechanical analysis (DMA) plot of compressive modulus as a function of temperature for PMI foam materials produced using thermal curing and photocuring compared to two different commercially available PMI foam materials.

[0026] FIG. 3 shows temperature measurements over time upon irradiation with a 810nm LED (0.95W/cm^2 irradiance) at the surface of precursor polymer samples without blowing agents and containing the NIR dye IR-813 at different %wt as compared to a control precursor polymer sample without the dye. Imidization temperatures can be reached in 50 s.

[0027] FIG. 4 shows temperature measurements over time upon irradiation with a 810 nm LED (1.31 W/cm^2 irradiance) at the surface of precursor polymer samples without blowing agents and containing the NIR dye IR-813 at different %wt as compared to a control precursor polymer sample without the dye. Minimal imidization temperatures can be reached in 30 s.

[0028] FIG. 5 shows temperature measurements over time upon irradiation with a 810 nm LED (0.95W/cm^2 irradiance) at the surface of foamable precursor polymer samples containing the NIR dye IR-813 at different %wt as compared to a control precursor polymer sample without the dye. The drop in temperature in the curve corresponds to the foaming onset at around 100 s.

[0029] FIG. 6 shows temperature measurements over time upon irradiation with a 810 nm LED (1.31W/cm^2 irradiance) at the surface of foamable precursor polymer samples containing the NIR dye IR-813 at different %wt as compared to a control precursor polymer sample without the dye. The drop in temperature in the curves corresponds to the foaming onset.

[0030] FIG. 7 shows temperature measurements over time upon irradiation with a 810 nm LED (1.48 W/cm^2 irradiance) at the surface of foamable precursor polymer samples containing the NIR dye IR-813 at different %wt as compared to a control precursor polymer sample without the dye. The drop in temperature in the curves corresponds to the foaming onset.

[0031] FIG. 8 shows temperature measurements over time upon irradiation with a 810 nm LED (0.95 W/cm^2 irradiance) at the surface of foamable precursor polymer samples containing the NIR dye IR-783 at different %wt as compared to a control precursor polymer sample without the dye. The drop in temperature in the curve corresponds to the foaming onset at around 60 s.

[0032] FIG. 9 shows temperature measurements over time upon irradiation with a 810 nm LED (1.31W/cm^2 irradiance) at the surface of foamable precursor polymer samples containing the NIR dye IR-783 at different %wt as compared to a control precursor polymer sample without the dye. The drop in temperature in the curves corresponds to the foaming onset.

[0033] FIG. 10 shows temperature measurements over time upon irradiation with a 810 nm LED (1.48 W/cm^2 irradiance) at the surface of foamable precursor polymer samples containing the NIR dye IR-783 at different %wt as compared to a control precursor polymer sample without the dye. The drop in temperature in the curves corresponds to the foaming onset.

DEFINITIONS

[0034] 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 Thomas Sorrell, *Organic Chemistry*, University Science Books, Sausalito, 1999;Michael B. Smith, *March's Advanced Organic Chemistry*, 7th Edition, John Wiley & Sons, Inc., New York, 2013; Richard C. Larock, *Comprehensive Organic Transformations*, John Wiley & Sons, Inc., New York, 2018; and Carruthers, Some Modern Methods of Organic Synthesis, 3rd Edition, Cambridge University Press, Cambridge, 1987.

[0035] A group is optionally substituted unless expressly provided otherwise. The term "optionally substituted" refers to being substituted or unsubstituted. In certain embodiments, alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl groups are optionally substituted. "Optionally substituted" refers to a group which is substituted or unsubstituted (*e.g.*, "substituted" or "unsubstituted" alkyl, "substituted" or "unsubstituted" alkenyl, "substituted" or "unsubstituted" alkynyl, "substituted" or "unsubstituted" heteroalkyl, "substituted" or "unsubstituted" heteroalkenyl, "substituted" or "unsubstituted" heteroalkynyl, "substituted" or "unsubstituted" carbocyclyl, "substituted" or "unsubstituted" heterocyclyl, "substituted" or "unsubstituted" aryl or "substituted" or "unsubstituted" heteroaryl group). In general, the term "substituted" means that at least one hydrogen present on a group is replaced with a permissible substituent, *e.g.*, a substituent which upon substitution results in a stable compound, *e.g.*, a compound which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, or other reaction.

[0036] Unless otherwise indicated, a "substituted" group has a substituent at one or more substitutable positions of the group, and when more than one position in any given structure is substituted, the substituent is either the same or different at each position. The term "substituted" is contemplated to include substitution with all permissible substituents of organic compounds, and includes any of the substituents described herein that results in the formation of a stable compound. The present disclosure contemplates any and all such combinations in order to arrive at a stable compound. For purposes of this disclosure, heteroatoms such as nitrogen may have hydrogen substituents and/or any suitable substituent as described herein which satisfy the valencies of the heteroatoms and results in the formation of a stable moiety. The disclosure is not limited in any manner by the exemplary substituents described herein.

[0037] In certain embodiments, each oxygen atom substituent is independently substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, $-C(=O)R^{aa}$, $-CO_2R^{aa}$, $-C(=O)N(R^{bb})_2$, or an oxygen protecting group. In certain embodiments, each oxygen atom substituents is independently substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-6} alkyl, $-C(=O)R^{aa}$, $-CO_2R^{aa}$, $-C(=O)N(R^{bb})_2$, or an oxygen protecting group, wherein R^{aa} is hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, or an oxygen protecting group when attached to an oxygen atom; and each R^{bb} is independently hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, or a nitrogen protecting group. In certain embodiments, each oxygen atom substituent is independently substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-6} alkyl or an oxygen protecting group.

[0038] In certain embodiments, the substituent present on an oxygen atom is an oxygen protecting group (also referred to herein as an "hydroxyl protecting group"). Oxygen protecting groups include $–R^{aa}$, $–N(R^{bb})_2$, $–C(=O)SR^{aa}$, $–C(=O)R^{aa}$, $–CO_2R^{aa}$, $–C(=O)N(R^{bb})_2$, $–C(=NR^{bb})R^{aa}$, $–C(=NR^{bb})OR^{aa}$, $–C(=NR^{bb})N(R^{bb})_2$, $–S(=O)R^{aa}$, $–SO_2R^{aa}$, $–Si(R^{aa})_3$, $–P(R^{cc})_2$, $–P(R^{cc})_3^+X^-$, $–P(OR^{cc})_2$, $–P(OR^{cc})_3^+X^-$, $–P(=O)(R^{aa})_2$, $–P(=O)(OR^{cc})_2$, and $–P(=O)(N(R^{bb})_2)_2$, wherein X^-, R^{aa}, R^{bb}, and R^{cc} are as defined herein. Oxygen protecting groups are well known in the art and include those described in detail in *Protecting Groups in Organic Synthesis*, T. W. Greene and P. G. M. Wuts, 3rd edition, John Wiley & Sons, 1999, incorporated herein by reference.

[0039] Nitrogen atoms can be substituted or unsubstituted as valency permits, and include primary, secondary, tertiary, and quaternary nitrogen atoms. Exemplary nitrogen atom substituents include hydrogen, $–OH$, $–OR^{aa}$, $–N(R^{cc})_2$, $–CN$, $–C(=O)R^{aa}$, $–C(=O)N(R^{cc})_2$, $–CO_2R^{aa}$, $–SO_2R^{aa}$, $–C(=NR^{bb})R^{aa}$, $–C(=NR^{cc})OR^{aa}$, $–C(=NR^{cc})N(R^{cc})_2$, $–SO_2N(R^{cc})_2$, $–SO_2R^{cc}$, $–SO_2OR^{cc}$, $–SOR^{aa}$, $–C(=S)N(R^{cc})_2$, $–C(=O)SR^{cc}$, $–C(=S)SR^{cc}$, $–P(=O)(OR^{cc})_2$, $–P(=O)(R^{aa})_2$, $–P(=O)(N(R^{cc})_2)_2$, $C_{1–20}$ alkyl, $C_{1–20}$ perhaloalkyl, $C_{1–20}$ alkenyl, $C_{1–20}$ alkynyl, hetero $C_{1–20}$ alkyl, hetero $C_{1–20}$ alkenyl, hetero $C_{1–20}$ alkynyl, C_{3-10} carbocyclyl, 3-14 membered heterocyclyl, C_{6-14} aryl, and 5-14 membered heteroaryl, or two R^{cc} groups attached to an N atom are joined to form a 3-14 membered heterocyclyl or 5-14 membered heteroaryl ring, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{dd} groups, and wherein R^{aa}, R^{bb}, R^{cc} and R^{dd} are as defined above.

[0040] In certain embodiments, each nitrogen atom substituent is independently substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-6} alkyl, $–C(=O)R^{aa}$, $–CO_2R^{aa}$, $–C(=O)N(R^{bb})_2$, or a nitrogen protecting group. In certain embodiments, each nitrogen atom substituent is independently substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, $–C(=O)R^{aa}$, $–CO_2R^{aa}$, $–C(=O)N(R^{bb})_2$, or a nitrogen protecting group, wherein R^{aa} is hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, or an oxygen protecting group when attached to an oxygen atom; and each R^{bb} is independently hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, or a nitrogen protecting group. In certain embodiments, each nitrogen atom substituent is independently substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-6} alkyl or a nitrogen protecting group.

[0041] In certain embodiments, the substituent present on the nitrogen atom is a nitrogen protecting group (also referred to herein as an “amino protecting group”). Nitrogen protecting groups include –OH, $–OR^{aa}$, $–N(R^{cc})_2$, $–C(=O)R^{aa}$, $–C(=O)N(R^{cc})_2$, $–CO_2R^{aa}$, $–SO_2R^{aa}$, $–C(=NR^{cc})R^{aa}$, $–C(=NR^{cc})OR^{aa}$, $–C(=NR^{cc})N(R^{cc})_2$, $–SO_2N(R^{cc})_2$, $–SO_2R^{cc}$, $–SO_2OR^{cc}$, $–SOR^{aa}$, $–C(=S)N(R^{cc})_2$, $–C(=O)SR^{cc}$, $–C(=S)SR^{cc}$, $C_{1–10}$ alkyl (*e.g.*, aralkyl, heteroaralkyl), $C_{1–20}$ alkenyl, $C_{1–20}$ alkynyl, hetero $C_{1–20}$ alkyl, hetero $C_{1–20}$ alkenyl, hetero $C_{1–20}$ alkynyl, C_{3-10} carbocyclyl, 3-14 membered heterocyclyl, C_{6-14} aryl, and 5-14 membered heteroaryl groups, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aralkyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{dd} groups, and wherein R^{aa}, R^{bb}, R^{cc} and R^{dd} are as defined herein. Nitrogen protecting groups are well known in the art and include those described in detail in *Protecting Groups in Organic Synthesis*, T. W. Greene and P. G. M. Wuts, 3rd edition, John Wiley & Sons, 1999, incorporated herein by reference.

[0042] Exemplary carbon atom substituents include halogen, –CN, $–NO_2$, $–N_3$, $–SO_2H$, $–SO_3H$, –OH, $–OR^{aa}$, $–ON(R^{bb})_2$, $–N(R^{bb})_2$, $–N(R^{bb})_3^+X^–$, $–N(OR^{cc})R^{bb}$, –SH, $–SR^{aa}$, $–SSR^{cc}$, $–C(=O)R^{aa}$, $–CO_2H$, –CHO, $–C(OR^{cc})_2$, $–CO_2R^{aa}$, $–OC(=O)R^{aa}$, $–OCO_2R^{aa}$, $–C(=O)N(R^{bb})_2$, $–OC(=O)N(R^{bb})_2$, $–NR^{bb}C(=O)R^{aa}$, $–NR^{bb}CO_2R^{aa}$, $–NR^{bb}C(=O)N(R^{bb})_2$, $–C(=NR^{bb})R^{aa}$, $–C(=NR^{bb})OR^{aa}$, $–OC(=NR^{bb})R^{aa}$, $–OC(=NR^{bb})OR^{aa}$, $–C(=NR^{bb})N(R^{bb})_2$, $–OC(=NR^{bb})N(R^{bb})_2$, $–NR^{bb}C(=NR^{bb})N(R^{bb})_2$, $–C(=O)NR^{bb}SO_2R^{aa}$, $–NR^{bb}SO_2R^{aa}$, $–SO_2N(R^{bb})_2$, $–SO_2R^{aa}$, $–SO_2OR^{aa}$, $–OSO_2R^{aa}$, $–S(=O)R^{aa}$, $–OS(=O)R^{aa}$, $–Si(R^{aa})_3$, $–OSi(R^{aa})_3$ $–C(=S)N(R^{bb})_2$, $–C(=O)SR^{aa}$, $–C(=S)SR^{aa}$, $–SC(=S)SR^{aa}$, $–SC(=O)SR^{aa}$, $–OC(=O)SR^{aa}$, $–SC(=O)OR^{aa}$, $–SC(=O)R^{aa}$, $–P(=O)(R^{aa})_2$, $–P(=O)(OR^{cc})_2$, $–OP(=O)(R^{aa})_2$, $–OP(=O)(OR^{cc})_2$, $–P(=O)(N(R^{bb})_2)_2$, $–OP(=O)(N(R^{bb})_2)_2$, $–NR^{bb}P(=O)(R^{aa})_2$, $–NR^{bb}P(=O)(OR^{cc})_2$, $–NR^{bb}P(=O)(N(R^{bb})_2)_2$, $–P(R^{cc})_2$, $–P(OR^{cc})_2$, $–P(R^{cc})_3^+X^–$, $–P(OR^{cc})_3^+X^–$, $–P(R^{cc})_4$, $–P(OR^{cc})_4$, $–OP(R^{cc})_2$, $–OP(R^{cc})_3^+X^–$, $–OP(OR^{cc})_2$, $–OP(OR^{cc})_3^+X^–$, $–OP(R^{cc})_4$, $–OP(OR^{cc})_4$, $–B(R^{aa})_2$, $–B(OR^{cc})_2$, $–BR^{aa}(OR^{cc})$, $C_{1–20}$ alkyl, $C_{1–20}$ perhaloalkyl, $C_{1–20}$ alkenyl, $C_{1–20}$ alkynyl, hetero$C_{1–20}$ alkyl, hetero$C_{1–20}$ alkenyl, hetero$C_{1–20}$ alkynyl, C_{3-10} carbocyclyl, 3-14 membered heterocyclyl, C_{6-14} aryl, and 5-14 membered heteroaryl, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{dd} groups; wherein $X^–$ is a counterion;

or two geminal hydrogens on a carbon atom are replaced with the group =O, =S, $=NN(R^{bb})_2$, $=NNR^{bb}C(=O)R^{aa}$, $=NNR^{bb}C(=O)OR^{aa}$, $=NNR^{bb}S(=O)_2R^{aa}$, $=NR^{bb}$, or $=NOR^{cc}$;

wherein:

each instance of R^{aa} is, independently, selected from C_{1-20} alkyl, C_{1-20} perhaloalkyl, C_{1-20} alkenyl, C_{1-20} alkynyl, heteroC_{1-20} alkyl, heteroC_{1-20}alkenyl, heteroC_{1-20}alkynyl, C_{3-10} carbocyclyl, 3-14 membered heterocyclyl, C_{6-14} aryl, and 5-14 membered heteroaryl, or two R^{aa} groups are joined to form a 3-14 membered heterocyclyl or 5-14 membered heteroaryl ring, wherein each of the alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{dd} groups;

each instance of R^{bb} is, independently, selected from hydrogen, –OH, $-OR^{aa}$, $-N(R^{cc})_2$, –CN, $-C(=O)R^{aa}$, $-C(=O)N(R^{cc})_2$, $-CO_2R^{aa}$, $-SO_2R^{aa}$, $-C(=NR^{cc})OR^{aa}$, $-C(=NR^{cc})N(R^{cc})_2$, $-SO_2N(R^{cc})_2$, $-SO_2R^{cc}$, $-SO_2OR^{cc}$, $-SOR^{aa}$, $-C(=S)N(R^{cc})_2$, $-C(=O)SR^{cc}$, $-C(=S)SR^{cc}$, $-P(=O)(R^{aa})_2$, $-P(=O)(OR^{cc})_2$, $-P(=O)(N(R^{cc})_2)_2$, C_{1-20} alkyl, C_{1-20} perhaloalkyl, C_{1-20} alkenyl, C_{1-20} alkynyl, heteroC_{1-20}alkyl, heteroC_{1-20}alkenyl, heteroC_{1-20}alkynyl, C_{3-10} carbocyclyl, 3-14 membered heterocyclyl, C_{6-14} aryl, and 5-14 membered heteroaryl, or two R^{bb} groups are joined to form a 3-14 membered heterocyclyl or 5-14 membered heteroaryl ring, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{dd} groups;

each instance of R^{cc} is, independently, selected from hydrogen, C_{1-20} alkyl, C_{1-20} perhaloalkyl, C_{1-20} alkenyl, C_{1-20} alkynyl, heteroC_{1-20} alkyl, heteroC_{1-20} alkenyl, heteroC_{1-20} alkynyl, C_{3-10} carbocyclyl, 3-14 membered heterocyclyl, C_{6-14} aryl, and 5-14 membered heteroaryl, or two R^{cc} groups are joined to form a 3-14 membered heterocyclyl or 5-14 membered heteroaryl ring, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{dd} groups;

each instance of R^{dd} is, independently, selected from halogen, –CN, $-NO_2$, $-N_3$, $-SO_2H$, $-SO_3H$, –OH, $-OR^{ee}$, $-ON(R^{ff})_2$, $-N(R^{ff})_2$, $-N(R^{ff})_3^+X^-$, $-N(OR^{ee})R^{ff}$, –SH, $-SR^{ee}$, $-SSR^{ee}$, $-C(=O)R^{ee}$, $-CO_2H$, $-CO_2R^{ee}$, $-OC(=O)R^{ee}$, $-OCO_2R^{ee}$, $-C(=O)N(R^{ff})_2$, $-OC(=O)N(R^{ff})_2$, $-NR^{ff}C(=O)R^{ee}$, $-NR^{ff}CO_2R^{ee}$, $-NR^{ff}C(=O)N(R^{ff})_2$, $-C(=NR^{ff})OR^{ee}$, $-OC(=NR^{ff})R^{ee}$, $-OC(=NR^{ff})OR^{ee}$, $-C(=NR^{ff})N(R^{ff})_2$, $-OC(=NR^{ff})N(R^{ff})_2$, $-NR^{ff}C(=NR^{ff})N(R^{ff})_2$, $-NR^{ff}SO_2R^{ee}$, $-SO_2N(R^{ff})_2$, $-SO_2R^{ee}$, $-SO_2OR^{ee}$, $-OSO_2R^{ee}$, $-S(=O)R^{ee}$, $-Si(R^{ee})_3$, $-OSi(R^{ee})_3$, $-C(=S)N(R^{ff})_2$,

–C(=O)SR^{ee}, –C(=S)SR^{ee}, –SC(=S)SR^{ee}, –P(=O)(OR^{ee})$_2$, –P(=O)(R^{ee})$_2$, –OP(=O)(R^{ee})$_2$, –OP(=O)(OR^{ee})$_2$, C$_{1–10}$ alkyl, C$_{1–10}$ perhaloalkyl, C$_{1–10}$ alkenyl, C$_{1–10}$ alkynyl, heteroC$_{1–10}$alkyl, heteroC$_{1–10}$alkenyl, heteroC$_{1–10}$alkynyl, C$_{3-10}$ carbocyclyl, 3-10 membered heterocyclyl, C$_{6-10}$ aryl, and 5-10 membered heteroaryl, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{gg} groups, or two geminal R^{dd} substituents are joined to form =O or =S; wherein X$^–$ is a counterion;

each instance of R^{ee} is, independently, selected from C$_{1–10}$ alkyl, C$_{1–10}$ perhaloalkyl, C$_{1–10}$ alkenyl, C$_{1–10}$ alkynyl, heteroC$_{1–10}$ alkyl, heteroC$_{1–10}$ alkenyl, heteroC$_{1–10}$ alkynyl, C$_{3-10}$ carbocyclyl, C$_{6-10}$ aryl, 3-10 membered heterocyclyl, and 3-10 membered heteroaryl, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{gg} groups;

each instance of R^{ff} is, independently, selected from hydrogen, C$_{1–10}$ alkyl, C$_{1–10}$ perhaloalkyl, C$_{1–10}$ alkenyl, C$_{1–10}$ alkynyl, heteroC$_{1–10}$ alkyl, heteroC$_{1–10}$ alkenyl, heteroC$_{1–10}$ alkynyl, C$_{3-10}$ carbocyclyl, 3-10 membered heterocyclyl, C$_{6-10}$ aryl, and 5-10 membered heteroaryl, or two R^{ff} groups are joined to form a 3-10 membered heterocyclyl or 5-10 membered heteroaryl ring, wherein each alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, carbocyclyl, heterocyclyl, aryl, and heteroaryl is independently substituted with 0, 1, 2, 3, 4, or 5 R^{gg} groups;

each instance of R^{gg} is, independently, halogen, –CN, –NO$_2$, –N$_3$, –SO$_2$H, –SO$_3$H, –OH, –OC$_{1–6}$ alkyl, –ON(C$_{1–6}$ alkyl)$_2$, –N(C$_{1–6}$ alkyl)$_2$, –N(C$_{1–6}$ alkyl)$_3$$^+X^–$, –NH(C$_{1–6}$ alkyl)$_2$$^+X^–$, –NH$_2$(C$_{1–6}$ alkyl) $^+$X$^–$, –NH$_3$$^+X^–$, –N(OC$_{1–6}$ alkyl)(C$_{1–6}$ alkyl), –N(OH)(C$_{1–6}$ alkyl), –NH(OH), –SH, –SC$_{1–6}$ alkyl, –SS(C$_{1–6}$ alkyl), –C(=O)(C$_{1–6}$ alkyl), –CO$_2$H, –CO$_2$(C$_{1–6}$ alkyl), –OC(=O)(C$_{1–6}$ alkyl), –OCO$_2$(C$_{1–6}$ alkyl), –C(=O)NH$_2$, –C(=O)N(C$_{1–6}$ alkyl)$_2$, –OC(=O)NH(C$_{1–6}$ alkyl), –NHC(=O)(C$_{1–6}$ alkyl), –N(C$_{1–6}$ alkyl)C(=O)(C$_{1–6}$ alkyl), –NHCO$_2$(C$_{1–6}$ alkyl), –NHC(=O)N(C$_{1–6}$ alkyl)$_2$, –NHC(=O)NH(C$_{1–6}$ alkyl), –NHC(=O)NH$_2$, –C(=NH)O(C$_{1–6}$ alkyl), –OC(=NH)(C$_{1–6}$ alkyl), –OC(=NH)OC$_{1–6}$ alkyl, –C(=NH)N(C$_{1–6}$ alkyl)$_2$, –C(=NH)NH(C$_{1–6}$ alkyl), –C(=NH)NH$_2$, –OC(=NH)N(C$_{1–6}$ alkyl)$_2$, –OC(NH)NH(C$_{1–6}$ alkyl), –OC(NH)NH$_2$, –NHC(NH)N(C$_{1–6}$ alkyl)$_2$, –NHC(=NH)NH$_2$, –NHSO$_2$(C$_{1–6}$ alkyl), –SO$_2$N(C$_{1–6}$ alkyl)$_2$, –SO$_2$NH(C$_{1–6}$ alkyl), –SO$_2$NH$_2$, –SO$_2$C$_{1–6}$ alkyl, –SO$_2$OC$_{1–6}$ alkyl, –OSO$_2$C$_{1–6}$ alkyl, –SOC$_{1–6}$ alkyl, –Si(C$_{1–6}$ alkyl)$_3$, –OSi(C$_{1–6}$

alkyl)$_3$ –C(=S)N(C$_{1-6}$ alkyl)$_2$, C(=S)NH(C$_{1-6}$ alkyl), C(=S)NH$_2$, –C(=O)S(C$_{1-6}$ alkyl), –C(=S)SC$_{1-6}$ alkyl, –SC(=S)SC$_{1-6}$ alkyl, –P(=O)(OC$_{1-6}$ alkyl)$_2$, –P(=O)(C$_{1-6}$ alkyl)$_2$, –OP(=O)(C$_{1-6}$ alkyl)$_2$, –OP(=O)(OC$_{1-6}$ alkyl)$_2$, C$_{1-10}$ alkyl, C$_{1-10}$ perhaloalkyl, C$_{1-10}$ alkenyl, C$_{1-10}$ alkynyl, heteroC$_{1-10}$ alkyl, heteroC$_{1-10}$ alkenyl, heteroC$_{1-10}$ alkynyl, C$_{3-10}$ carbocyclyl, C$_{6-10}$ aryl, 3-10 membered heterocyclyl, or 5-10 membered heteroaryl; or two geminal R^{gg} substituents can be joined to form =O or =S; and

each X$^-$ is a counterion.

[0043] In certain embodiments, each carbon atom substituent is independently halogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C$_{1-6}$ alkyl, –OR^{aa}, –SR^{aa}, –N(R^{bb})$_2$, –CN, –SCN, –NO$_2$, –C(=O)R^{aa}, –CO$_2$R^{aa}, –C(=O)N(R^{bb})$_2$, –OC(=O)R^{aa}, –OCO$_2$R^{aa}, –OC(=O)N(R^{bb})$_2$, –NR^{bb}C(=O)R^{aa}, –NR^{bb}CO$_2$R^{aa}, or –NR^{bb}C(=O)N(R^{bb})$_2$. In certain embodiments, each carbon atom substituent is independently halogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C$_{1-10}$ alkyl, –OR^{aa}, –SR^{aa}, –N(R^{bb})$_2$, –CN, –SCN, –NO$_2$, –C(=O)R^{aa}, –CO$_2$R^{aa}, –C(=O)N(R^{bb})$_2$, –OC(=O)R^{aa}, –OCO$_2$R^{aa}, –OC(=O)N(R^{bb})$_2$, –NR^{bb}C(=O)R^{aa}, –NR^{bb}CO$_2$R^{aa}, or –NR^{bb}C(=O)N(R^{bb})$_2$, wherein R^{aa} is hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C$_{1-10}$ alkyl, an oxygen protecting group (*e.g.*, silyl, TBDPS, TBDMS, TIPS, TES, TMS, MOM, THP, t-Bu, Bn, allyl, acetyl, pivaloyl, or benzoyl) when attached to an oxygen atom, or a sulfur protecting group (*e.g.*, acetamidomethyl, t-Bu, 3-nitro-2-pyridine sulfenyl, 2-pyridine-sulfenyl, or triphenylmethyl) when attached to a sulfur atom; and each R^{bb} is independently hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C$_{1-10}$ alkyl, or a nitrogen protecting group (*e.g.*, Bn, Boc, Cbz, Fmoc, trifluoroacetyl, triphenylmethyl, acetyl, or Ts). In certain embodiments, each carbon atom substituent is independently halogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C$_{1-6}$ alkyl, –OR^{aa}, –SR^{aa}, –N(R^{bb})$_2$, –CN, –SCN, or –NO$_2$. In certain embodiments, each carbon atom substituent is independently halogen, substituted (*e.g.*, substituted with one or more halogen moieties) or unsubstituted C$_{1-10}$ alkyl, –OR^{aa}, –SR^{aa}, –N(R^{bb})$_2$, –CN, –SCN, or –NO$_2$, wherein R^{aa} is hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C$_{1-10}$ alkyl, an oxygen protecting group (*e.g.*, silyl, TBDPS, TBDMS, TIPS, TES, TMS, MOM, THP, t-Bu, Bn, allyl, acetyl, pivaloyl, or benzoyl) when attached to an oxygen atom, or a sulfur protecting group (*e.g.*, acetamidomethyl, t-Bu, 3-nitro-2-pyridine sulfenyl, 2-pyridine-sulfenyl, or triphenylmethyl) when attached to a sulfur atom; and each R^{bb} is independently hydrogen, substituted (*e.g.*, substituted with one or more halogen) or unsubstituted C_{1-10} alkyl, or a nitrogen protecting group (*e.g.*, Bn, Boc, Cbz, Fmoc, trifluoroacetyl, triphenylmethyl, acetyl, or Ts).

[0044] In certain embodiments, the molecular weight of an optional substituent is lower than 250, lower than 200, lower than 150, lower than 100, or lower than 50 g/mol.

[0045] Compounds described herein can comprise one or more asymmetric centers, and thus can exist in various stereoisomeric forms, *e.g.*, enantiomers and/or diastereomers. For example, the compounds described herein can be in the form of an individual enantiomer, diastereomer or geometric isomer, or can be in the form of a mixture of stereoisomers, including racemic mixtures and mixtures enriched in one or more stereoisomer. Isomers can be isolated from mixtures by methods known to those skilled in the art, including chiral high pressure liquid chromatography (HPLC) and the formation and crystallization of chiral salts; or preferred isomers can be prepared by asymmetric syntheses. See, for example, Jacques *et al.*, *Enantiomers, Racemates and Resolutions* (Wiley Interscience, New York, 1981); Wilen *et al.*, Tetrahedron 33:2725 (1977); Eliel, E.L. *Stereochemistry of Carbon Compounds* (McGraw–Hill, NY, 1962); and Wilen, S.H., *Tables of Resolving Agents and Optical Resolutions* p. 268 (E.L. Eliel, Ed., Univ. of Notre Dame Press, Notre Dame, IN 1972). The invention additionally encompasses compounds as individual isomers substantially free of other isomers, and alternatively, as mixtures of various isomers.

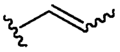
[0046] When a range of values is listed, it is intended to encompass each value and sub-range within the range. A range is inclusive of the values at the two ends of the range unless otherwise provided. For example, "C_{1-6} alkyl" encompasses, C_1, C_2, C_3, C_4, C_5, C_6, C_{1-6}, C_{1-5}, C_{1-4}, C_{1-3}, C_{1-2}, C_{2-6}, C_{2-5}, C_{2-4}, C_{2-3}, C_{3-6}, C_{3-5}, C_{3-4}, C_{4-6}, C_{4-5}, and C_{5-6} alkyl.

[0047] The term "aliphatic" refers to alkyl, alkenyl, alkynyl, and carbocyclic groups. Likewise, the term "heteroaliphatic" refers to heteroalkyl, heteroalkenyl, heteroalkynyl, and heterocyclic groups.

[0048] The term "alkyl" refers to a radical of a straight-chain or branched saturated hydrocarbon group having from 1 to 20 carbon atoms ("C_{1-20} alkyl"). In some embodiments, an alkyl group has 1 to 12 carbon atoms ("C_{1-12} alkyl"). In some embodiments, an alkyl group has 1 to 10 carbon atoms ("C_{1-10} alkyl"). In some embodiments, an alkyl group has 1 to 9 carbon atoms ("C_{1-9} alkyl"). In some embodiments, an alkyl group has 1 to 8 carbon atoms ("C_{1-8} alkyl"). In some embodiments, an alkyl group has 1 to 7 carbon atoms ("C_{1-7} alkyl"). In some embodiments, an alkyl group has 1 to 6 carbon atoms ("C_{1-6} alkyl"). In some embodiments, an alkyl group has 1 to 5 carbon atoms ("C_{1-5} alkyl"). In some embodiments, an alkyl group has 1 to 4 carbon atoms ("C_{1-4} alkyl"). In some embodiments, an alkyl group has 1 to 3 carbon atoms ("C_{1-3} alkyl"). In some embodiments, an alkyl group has 1 to 2 carbon atoms ("C_{1-2} alkyl"). In some embodiments, an alkyl group has 1 carbon atom ("C_1 alkyl"). In some embodiments, an alkyl group has 2 to 6 carbon atoms ("C_{2-6} alkyl"). Examples of C_{1-6} alkyl groups include methyl (C_1), ethyl (C_2), propyl (C_3) (*e.g.*, *n*-propyl, isopropyl), butyl (C_4) (*e.g.*, *n*-butyl, *tert*-butyl, *sec*-butyl, isobutyl), pentyl (C_5) (*e.g.*, *n*-pentyl, 3-pentanyl, amyl, neopentyl, 3-methyl-2-butanyl, *tert*-amyl), and hexyl (C_6) (*e.g.*, *n*-hexyl). Additional examples of alkyl groups include *n*-heptyl (C_7), *n*-octyl (C_8), *n*-dodecyl (C_{12}), and the like. Unless otherwise specified, each instance of an alkyl group is independently unsubstituted (an "unsubstituted alkyl") or substituted (a "substituted alkyl") with one or more substituents (*e.g.*, halogen, such as F). In certain embodiments, the alkyl group is an unsubstituted C_{1-12} alkyl (such as unsubstituted C_{1-6} alkyl, *e.g.*, $-CH_3$ (Me), unsubstituted ethyl (Et), unsubstituted propyl (Pr, *e.g.*, unsubstituted n-propyl (n-Pr), unsubstituted isopropyl (*i*-Pr)), unsubstituted butyl (Bu, *e.g.*, unsubstituted *n*-butyl (*n*-Bu), unsubstituted *tert*-butyl (*tert*-Bu or *t*-Bu), unsubstituted *sec*-butyl (*sec*-Bu or *s*-Bu), unsubstituted isobutyl (*i*-Bu)). In certain embodiments, the alkyl group is a substituted C_{1-12} alkyl (such as substituted C_{1-6} alkyl, *e.g.*, $-CH_2F$, $-CHF_2$, $-CF_3$, $-CH_2CH_2F$, $-CH_2CHF_2$, $-CH_2CF_3$, or benzyl (Bn)).

[0049] The term "heteroalkyl" refers to an alkyl group, which further includes at least one heteroatom (*e.g.*, 1, 2, 3, or 4 heteroatoms) selected from oxygen, nitrogen, or sulfur within (*e.g.*, inserted between adjacent carbon atoms of) and/or placed at one or more terminal position(s) of the parent chain. In certain embodiments, a heteroalkyl group refers to a saturated group having from 1 to 20 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-20} alkyl"). In certain embodiments, a heteroalkyl group refers to a saturated group having from 1 to 12 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-12} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 11 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-11} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 10 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-10} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 9 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-9} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 8 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-8} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 7 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-7} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 6 carbon atoms and 1 or more heteroatoms within the parent chain ("heteroC_{1-6} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 5 carbon atoms and 1 or 2 heteroatoms within the parent chain ("heteroC_{1-5} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 4 carbon atoms and 1or 2 heteroatoms within the parent chain ("heteroC_{1-4} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 3 carbon atoms and 1 heteroatom within the parent chain ("heteroC_{1-3} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 to 2 carbon atoms and 1 heteroatom within the parent chain ("heteroC_{1-2} alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 1 carbon atom and 1 heteroatom ("heteroC_1 alkyl"). In some embodiments, a heteroalkyl group is a saturated group having 2 to 6 carbon atoms and 1 or 2 heteroatoms within the parent chain ("heteroC_{2-6} alkyl"). Unless otherwise specified, each instance of a heteroalkyl group is independently unsubstituted (an "unsubstituted heteroalkyl") or substituted (a "substituted heteroalkyl") with one or more substituents. In certain embodiments, the heteroalkyl group is an unsubstituted heteroC_{1-12} alkyl. In certain embodiments, the heteroalkyl group is a substituted heteroC_{1-12} alkyl.

[0050] The term "alkenyl" refers to a radical of a straight-chain or branched hydrocarbon group having from 1 to 20 carbon atoms and one or more carbon-carbon double bonds (*e.g.*, 1, 2, 3, or 4 double bonds). In some embodiments, an alkenyl group has 1 to 20 carbon atoms ("C_{1-20} alkenyl"). In some embodiments, an alkenyl group has 1 to 12 carbon atoms ("C_{1-12} alkenyl"). In some embodiments, an alkenyl group has 1 to 11 carbon atoms ("C_{1-11} alkenyl"). In some embodiments, an alkenyl group has 1 to 10 carbon atoms ("C_{1-10} alkenyl"). In some embodiments, an alkenyl group has 1 to 9 carbon atoms ("C_{1-9} alkenyl"). In some embodiments, an alkenyl group has 1 to 8 carbon atoms ("C_{1-8} alkenyl"). In some embodiments, an alkenyl group has 1 to 7 carbon atoms ("C_{1-7} alkenyl"). In some embodiments, an alkenyl group has 1 to 6 carbon atoms ("C_{1-6} alkenyl"). In some embodiments, an alkenyl group has 1 to 5 carbon atoms ("C_{1-5} alkenyl"). In some embodiments, an alkenyl group has 1 to 4 carbon atoms ("C_{1-4} alkenyl"). In some embodiments, an alkenyl group has 1 to 3 carbon atoms ("C_{1-3} alkenyl"). In some embodiments, an alkenyl group has 1 to 2 carbon atoms ("C_{1-2} alkenyl"). In some embodiments, an alkenyl group has 1 carbon atom ("C_1 alkenyl"). The one or more carbon-carbon double bonds can be internal (such as in 2-butenyl) or terminal (such as in 1-butenyl). Examples of C_{1-4} alkenyl groups include methylidenyl (C_1), ethenyl (C_2), 1-propenyl (C_3), 2-propenyl (C_3), 1-butenyl (C_4), 2-butenyl (C_4), butadienyl (C_4), and the like. Examples of C_{1-6}

alkenyl groups include the aforementioned C_{2-4} alkenyl groups as well as pentenyl (C_5), pentadienyl (C_5), hexenyl (C_6), and the like. Additional examples of alkenyl include heptenyl (C_7), octenyl (C_8), octatrienyl (C_8), and the like. Unless otherwise specified, each instance of an alkenyl group is independently unsubstituted (an "unsubstituted alkenyl") or substituted (a "substituted alkenyl") with one or more substituents. In certain embodiments, the alkenyl group is an unsubstituted C_{1-20} alkenyl. In certain embodiments, the alkenyl group is a substituted C_{1-20} alkenyl. In an alkenyl group, a C=C double bond for which the stereochemistry is not specified (*e.g.*, –CH=$CHCH_3$ or ) may be in the (*E*)- or (*Z*)-configuration.

[0051] The term "heteroalkenyl" refers to an alkenyl group, which further includes at least one heteroatom (*e.g.*, 1, 2, 3, or 4 heteroatoms) selected from oxygen, nitrogen, or sulfur within (*e.g.*, inserted between adjacent carbon atoms of) and/or placed at one or more terminal position(s) of the parent chain. In certain embodiments, a heteroalkenyl group refers to a group having from 1 to 20 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-20} alkenyl"). In certain embodiments, a heteroalkenyl group refers to a group having from 1 to 12 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-12} alkenyl"). In certain embodiments, a heteroalkenyl group refers to a group having from 1 to 11 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-11} alkenyl"). In certain embodiments, a heteroalkenyl group refers to a group having from 1 to 10 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-10} alkenyl"). In some embodiments, a heteroalkenyl group has 1 to 9 carbon atoms at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-9} alkenyl"). In some embodiments, a heteroalkenyl group has 1 to 8 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-8} alkenyl"). In some embodiments, a heteroalkenyl group has 1 to 7 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-7} alkenyl"). In some embodiments, a heteroalkenyl group has 1to 6 carbon atoms, at least one double bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-6} alkenyl"). In some embodiments, a heteroalkenyl group has 1 to 5 carbon atoms, at least one double bond, and 1 or 2 heteroatoms within the parent chain ("heteroC_{1-5} alkenyl"). In some embodiments, a heteroalkenyl group has 1 to 4 carbon atoms, at least one double bond, and 1 or 2 heteroatoms within the parent chain ("heteroC_{1-4} alkenyl"). In some embodiments, a heteroalkenyl group has 1 to 3 carbon atoms, at least one double bond, and 1 heteroatom within the parent chain (“heteroC_{1-3} alkenyl”). In some embodiments, a heteroalkenyl group has 1 to 2 carbon atoms, at least one double bond, and 1 heteroatom within the parent chain (“heteroC_{1-2} alkenyl”). In some embodiments, a heteroalkenyl group has 1 to 6 carbon atoms, at least one double bond, and 1 or 2 heteroatoms within the parent chain (“heteroC_{1-6} alkenyl”). Unless otherwise specified, each instance of a heteroalkenyl group is independently unsubstituted (an “unsubstituted heteroalkenyl”) or substituted (a “substituted heteroalkenyl”) with one or more substituents. In certain embodiments, the heteroalkenyl group is an unsubstituted heteroC_{1-20} alkenyl. In certain embodiments, the heteroalkenyl group is a substituted heteroC_{1-20} alkenyl.

[0052] The term “alkynyl” refers to a radical of a straight-chain or branched hydrocarbon group having from 1 to 20 carbon atoms and one or more carbon-carbon triple bonds (*e.g.*, 1, 2, 3, or 4 triple bonds) (“C_{1-20} alkynyl”). In some embodiments, an alkynyl group has 1 to 10 carbon atoms (“C_{1-10} alkynyl”). In some embodiments, an alkynyl group has 1 to 9 carbon atoms (“C_{1-9} alkynyl”). In some embodiments, an alkynyl group has 1 to 8 carbon atoms (“C_{1-8} alkynyl”). In some embodiments, an alkynyl group has 1 to 7 carbon atoms (“C_{1-7} alkynyl”). In some embodiments, an alkynyl group has 1 to 6 carbon atoms (“C_{1-6} alkynyl”). In some embodiments, an alkynyl group has 1 to 5 carbon atoms (“C_{1-5} alkynyl”). In some embodiments, an alkynyl group has 1 to 4 carbon atoms (“C_{1-4} alkynyl”). In some embodiments, an alkynyl group has 1 to 3 carbon atoms (“C_{1-3} alkynyl”). In some embodiments, an alkynyl group has 1 to 2 carbon atoms (“C_{1-2} alkynyl”). In some embodiments, an alkynyl group has 1 carbon atom (“C_1 alkynyl”). The one or more carbon-carbon triple bonds can be internal (such as in 2-butynyl) or terminal (such as in 1-butynyl). Examples of C_{1-4} alkynyl groups include, without limitation, methylidynyl (C_1), ethynyl (C_2), 1-propynyl (C_3), 2-propynyl (C_3), 1-butynyl (C_4), 2-butynyl (C_4), and the like. Examples of C_{1-6} alkenyl groups include the aforementioned C_{2-4} alkynyl groups as well as pentynyl (C_5), hexynyl (C_6), and the like. Additional examples of alkynyl include heptynyl (C_7), octynyl (C_8), and the like. Unless otherwise specified, each instance of an alkynyl group is independently unsubstituted (an “unsubstituted alkynyl”) or substituted (a “substituted alkynyl”) with one or more substituents. In certain embodiments, the alkynyl group is an unsubstituted C_{1-20} alkynyl. In certain embodiments, the alkynyl group is a substituted C_{1-20} alkynyl.

[0053] The term “heteroalkynyl” refers to an alkynyl group, which further includes at least one heteroatom (*e.g.*, 1, 2, 3, or 4 heteroatoms) selected from oxygen, nitrogen, or sulfur within (*e.g.*, inserted between adjacent carbon atoms of) and/or placed at one or more terminal position(s) of the parent chain. In certain embodiments, a heteroalkynyl group refers to a group having from 1 to 20 carbon atoms, at least one triple bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-20} alkynyl"). In certain embodiments, a heteroalkynyl group refers to a group having from 1 to 10 carbon atoms, at least one triple bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-10} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 9 carbon atoms, at least one triple bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-9} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 8 carbon atoms, at least one triple bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-8} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 7 carbon atoms, at least one triple bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-7} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 6 carbon atoms, at least one triple bond, and 1 or more heteroatoms within the parent chain ("heteroC_{1-6} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 5 carbon atoms, at least one triple bond, and 1 or 2 heteroatoms within the parent chain ("heteroC_{1-5} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 4 carbon atoms, at least one triple bond, and 1or 2 heteroatoms within the parent chain ("heteroC_{1-4} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 3 carbon atoms, at least one triple bond, and 1 heteroatom within the parent chain ("heteroC_{1-3} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 2 carbon atoms, at least one triple bond, and 1 heteroatom within the parent chain ("heteroC_{1-2} alkynyl"). In some embodiments, a heteroalkynyl group has 1 to 6 carbon atoms, at least one triple bond, and 1 or 2 heteroatoms within the parent chain ("heteroC_{1-6} alkynyl"). Unless otherwise specified, each instance of a heteroalkynyl group is independently unsubstituted (an "unsubstituted heteroalkynyl") or substituted (a "substituted heteroalkynyl") with one or more substituents. In certain embodiments, the heteroalkynyl group is an unsubstituted heteroC_{1-20} alkynyl. In certain embodiments, the heteroalkynyl group is a substituted heteroC_{1-20} alkynyl.

[0054] The term "carbocyclyl" or "carbocyclic" refers to a radical of a non-aromatic cyclic hydrocarbon group having from 3 to 14 ring carbon atoms ("C_{3-14} carbocyclyl") and zero heteroatoms in the non-aromatic ring system. In some embodiments, a carbocyclyl group has 3 to 14 ring carbon atoms ("C_{3-14} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 13 ring carbon atoms ("C_{3-13} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 12 ring carbon atoms ("C_{3-12} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 11 ring carbon atoms ("C_{3-11} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 10 ring carbon atoms ("C_{3-10} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 8 ring carbon atoms ("C_{3-8} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 7 ring carbon atoms ("C_{3-7} carbocyclyl"). In some embodiments, a carbocyclyl group has 3 to 6 ring carbon atoms ("C_{3-6} carbocyclyl"). In some embodiments, a carbocyclyl group has 4 to 6 ring carbon atoms ("C_{4-6} carbocyclyl"). In some embodiments, a carbocyclyl group has 5 to 6 ring carbon atoms ("C_{5-6} carbocyclyl"). In some embodiments, a carbocyclyl group has 5 to 10 ring carbon atoms ("C_{5-10} carbocyclyl"). Exemplary C_{3-6} carbocyclyl groups include cyclopropyl (C_3), cyclopropenyl (C_3), cyclobutyl (C_4), cyclobutenyl (C_4), cyclopentyl (C_5), cyclopentenyl (C_5), cyclohexyl (C_6), cyclohexenyl (C_6), cyclohexadienyl (C_6), and the like. Exemplary C_{3-8} carbocyclyl groups include the aforementioned C_{3-6} carbocyclyl groups as well as cycloheptyl (C_7), cycloheptenyl (C_7), cycloheptadienyl (C_7), cycloheptatrienyl (C_7), cyclooctyl (C_8), cyclooctenyl (C_8), bicyclo[2.2.1]heptanyl (C_7), bicyclo[2.2.2]octanyl (C_8), and the like. Exemplary C_{3-10} carbocyclyl groups include the aforementioned C_{3-8} carbocyclyl groups as well as cyclononyl (C_9), cyclononenyl (C_9), cyclodecyl (C_{10}), cyclodecenyl (C_{10}), octahydro-1*H*-indenyl (C_9), decahydronaphthalenyl (C_{10}), spiro[4.5]decanyl (C_{10}), and the like. Exemplary C_{3-8} carbocyclyl groups include the aforementioned C_{3-10} carbocyclyl groups as well as cycloundecyl (C_{11}), spiro[5.5]undecanyl (C_{11}), cyclododecyl (C_{12}), cyclododecenyl (C_{12}), cyclotridecane (C_{13}), cyclotetradecane (C_{14}), and the like. As the foregoing examples illustrate, in certain embodiments, the carbocyclyl group is either monocyclic ("monocyclic carbocyclyl") or polycyclic (*e.g.*, containing a fused, bridged or spiro ring system such as a bicyclic system ("bicyclic carbocyclyl") or tricyclic system ("tricyclic carbocyclyl")) and can be saturated or can contain one or more carbon-carbon double or triple bonds. "Carbocyclyl" also includes ring systems wherein the carbocyclyl ring, as defined above, is fused with one or more aryl or heteroaryl groups wherein the point of attachment is on the carbocyclyl ring, and in such instances, the number of carbons continue to designate the number of carbons in the carbocyclic ring system. Unless otherwise specified, each instance of a carbocyclyl group is independently unsubstituted (an "unsubstituted carbocyclyl") or substituted (a "substituted carbocyclyl") with one or more substituents. In certain embodiments, the carbocyclyl group is an unsubstituted C_{3-14} carbocyclyl. In certain embodiments, the carbocyclyl group is a substituted C_{3-14} carbocyclyl.

[0055] In some embodiments, "carbocyclyl" is a monocyclic, saturated carbocyclyl group having from 3 to 14 ring carbon atoms ("C_{3-14} cycloalkyl"). In some embodiments, a cycloalkyl group has 3 to 10 ring carbon atoms ("C_{3-10} cycloalkyl"). In some embodiments, a cycloalkyl group has 3 to 8 ring carbon atoms (“C_{3-8} cycloalkyl”). In some embodiments, a cycloalkyl group has 3 to 6 ring carbon atoms (“C_{3-6} cycloalkyl”). In some embodiments, a cycloalkyl group has 4 to 6 ring carbon atoms (“C_{4-6} cycloalkyl”). In some embodiments, a cycloalkyl group has 5 to 6 ring carbon atoms (“C_{5-6} cycloalkyl”). In some embodiments, a cycloalkyl group has 5 to 10 ring carbon atoms (“C_{5-10} cycloalkyl”). Examples of C_{5-6} cycloalkyl groups include cyclopentyl (C_5) and cyclohexyl (C_5). Examples of C_{3-6} cycloalkyl groups include the aforementioned C_{5-6} cycloalkyl groups as well as cyclopropyl (C_3) and cyclobutyl (C_4). Examples of C_{3-8} cycloalkyl groups include the aforementioned C_{3-6} cycloalkyl groups as well as cycloheptyl (C_7) and cyclooctyl (C_8). Unless otherwise specified, each instance of a cycloalkyl group is independently unsubstituted (an “unsubstituted cycloalkyl”) or substituted (a “substituted cycloalkyl”) with one or more substituents. In certain embodiments, the cycloalkyl group is an unsubstituted C_{3-14} cycloalkyl. In certain embodiments, the cycloalkyl group is a substituted C_{3-14} cycloalkyl. In certain embodiments, the carbocyclyl includes 0, 1, or 2 C=C double bonds in the carbocyclic ring system, as valency permits.

[0056] The term “heterocyclyl” or “heterocyclic” refers to a radical of a 3- to 14-membered non-aromatic ring system having ring carbon atoms and 1 to 4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur (“3–14 membered heterocyclyl”). In heterocyclyl groups that contain one or more nitrogen atoms, the point of attachment can be a carbon or nitrogen atom, as valency permits. A heterocyclyl group can either be monocyclic (“monocyclic heterocyclyl”) or polycyclic (*e.g.*, a fused, bridged or spiro ring system such as a bicyclic system (“bicyclic heterocyclyl”) or tricyclic system (“tricyclic heterocyclyl”)), and can be saturated or can contain one or more carbon-carbon double or triple bonds. Heterocyclyl polycyclic ring systems can include one or more heteroatoms in one or both rings. “Heterocyclyl” also includes ring systems wherein the heterocyclyl ring, as defined above, is fused with one or more carbocyclyl groups wherein the point of attachment is either on the carbocyclyl or heterocyclyl ring, or ring systems wherein the heterocyclyl ring, as defined above, is fused with one or more aryl or heteroaryl groups, wherein the point of attachment is on the heterocyclyl ring, and in such instances, the number of ring members continue to designate the number of ring members in the heterocyclyl ring system. Unless otherwise specified, each instance of heterocyclyl is independently unsubstituted (an “unsubstituted heterocyclyl”) or substituted (a “substituted heterocyclyl”) with one or more substituents. In certain embodiments, the heterocyclyl group is an unsubstituted 3–14 membered heterocyclyl. In certain embodiments, the heterocyclyl group is a substituted 3–14 membered heterocyclyl. In certain embodiments, the heterocyclyl is substituted or unsubstituted, 3- to 7-membered, monocyclic heterocyclyl, wherein 1, 2, or 3 atoms in the heterocyclic ring system are independently oxygen, nitrogen, or sulfur, as valency permits.

[0057] In some embodiments, a heterocyclyl group is a 5–10 membered non-aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur ("5–10 membered heterocyclyl"). In some embodiments, a heterocyclyl group is a 5–8 membered non-aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur ("5–8 membered heterocyclyl"). In some embodiments, a heterocyclyl group is a 5–6 membered non-aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur ("5–6 membered heterocyclyl"). In some embodiments, the 5–6 membered heterocyclyl has 1–3 ring heteroatoms selected from nitrogen, oxygen, and sulfur. In some embodiments, the 5–6 membered heterocyclyl has 1–2 ring heteroatoms selected from nitrogen, oxygen, and sulfur. In some embodiments, the 5–6 membered heterocyclyl has 1 ring heteroatom selected from nitrogen, oxygen, and sulfur.

[0058] Exemplary 3-membered heterocyclyl groups containing 1 heteroatom include azirdinyl, oxiranyl, and thiiranyl. Exemplary 4-membered heterocyclyl groups containing 1 heteroatom include azetidinyl, oxetanyl, and thietanyl. Exemplary 5-membered heterocyclyl groups containing 1 heteroatom include tetrahydrofuranyl, dihydrofuranyl, tetrahydrothiophenyl, dihydrothiophenyl, pyrrolidinyl, dihydropyrrolyl, and pyrrolyl-2,5-dione. Exemplary 5-membered heterocyclyl groups containing 2 heteroatoms include dioxolanyl, oxathiolanyl and dithiolanyl. Exemplary 5-membered heterocyclyl groups containing 3 heteroatoms include triazolinyl, oxadiazolinyl, and thiadiazolinyl. Exemplary 6-membered heterocyclyl groups containing 1 heteroatom include piperidinyl, tetrahydropyranyl, dihydropyridinyl, and thianyl. Exemplary 6-membered heterocyclyl groups containing 2 heteroatoms include piperazinyl, morpholinyl, dithianyl, and dioxanyl. Exemplary 6-membered heterocyclyl groups containing 3 heteroatoms include triazinyl. Exemplary 7-membered heterocyclyl groups containing 1 heteroatom include azepanyl, oxepanyl and thiepanyl. Exemplary 8-membered heterocyclyl groups containing 1 heteroatom include azocanyl, oxecanyl and thiocanyl. Exemplary bicyclic heterocyclyl groups include indolinyl, isoindolinyl, dihydrobenzofuranyl, dihydrobenzothienyl, tetrahydrobenzothienyl, tetrahydrobenzofuranyl, tetrahydroindolyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, decahydroquinolinyl, decahydroisoquinolinyl, octahydrochromenyl, octahydroisochromenyl, decahydronaphthyridinyl, decahydro-1,8-naphthyridinyl, octahydropyrrolo[3,2-b]pyrrole, indolinyl, phthalimidyl, naphthalimidyl, chromanyl, chromenyl, 1H-benzo[e][1,4]diazepinyl, 1,4,5,7-tetrahydropyrano[3,4-b]pyrrolyl, 5,6-dihydro-4H-furo[3,2-b]pyrrolyl, 6,7-dihydro-5H-furo[3,2-b]pyranyl, 5,7-dihydro-4H-thieno[2,3-c]pyranyl, 2,3-dihydro-1H-pyrrolo[2,3-b]pyridinyl, 2,3-dihydrofuro[2,3-b]pyridinyl, 4,5,6,7-tetrahydro-1H-pyrrolo[2,3-b]pyridinyl, 4,5,6,7-tetrahydrofuro[3,2-c]pyridinyl, 4,5,6,7-tetrahydrothieno[3,2-b]pyridinyl, 1,2,3,4-tetrahydro-1,6-naphthyridinyl, and the like.

[0059] The term “aryl” refers to a radical of a monocyclic or polycyclic (*e.g.*, bicyclic or tricyclic) 4n+2 aromatic ring system (*e.g.*, having 6, 10, or 14 □ electrons shared in a cyclic array) having 6–14 ring carbon atoms and zero heteroatoms provided in the aromatic ring system (“C_{6-14} aryl”). In some embodiments, an aryl group has 6 ring carbon atoms (“C_6 aryl”; *e.g.*, phenyl). In some embodiments, an aryl group has 10 ring carbon atoms (“C_{10} aryl”; *e.g.*, naphthyl such as 1–naphthyl and 2-naphthyl). In some embodiments, an aryl group has 14 ring carbon atoms (“C_{14} aryl”; *e.g.*, anthracyl). “Aryl” also includes ring systems wherein the aryl ring, as defined above, is fused with one or more carbocyclyl or heterocyclyl groups wherein the radical or point of attachment is on the aryl ring, and in such instances, the number of carbon atoms continue to designate the number of carbon atoms in the aryl ring system. Unless otherwise specified, each instance of an aryl group is independently unsubstituted (an “unsubstituted aryl”) or substituted (a “substituted aryl”) with one or more substituents. In certain embodiments, the aryl group is an unsubstituted C_{6-14} aryl. In certain embodiments, the aryl group is a substituted C_{6-14} aryl.

[0060] The term “heteroaryl” refers to a radical of a 5-14 membered monocyclic or polycyclic (*e.g.*, bicyclic, tricyclic) 4n+2 aromatic ring system (*e.g.*, having 6, 10, or 14 □ electrons shared in a cyclic array) having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur (“5-14 membered heteroaryl”). In heteroaryl groups that contain one or more nitrogen atoms, the point of attachment can be a carbon or nitrogen atom, as valency permits. Heteroaryl polycyclic ring systems can include one or more heteroatoms in one or both rings. “Heteroaryl” includes ring systems wherein the heteroaryl ring, as defined above, is fused with one or more carbocyclyl or heterocyclyl groups wherein the point of attachment is on the heteroaryl ring, and in such instances, the number of ring members continue to designate the number of ring members in the heteroaryl ring system.

"Heteroaryl" also includes ring systems wherein the heteroaryl ring, as defined above, is fused with one or more aryl groups wherein the point of attachment is either on the aryl or heteroaryl ring, and in such instances, the number of ring members designates the number of ring members in the fused polycyclic (aryl/heteroaryl) ring system. Polycyclic heteroaryl groups wherein one ring does not contain a heteroatom (*e.g.*, indolyl, quinolinyl, carbazolyl, and the like) the point of attachment can be on either ring, *e.g.*, either the ring bearing a heteroatom (*e.g.*, 2-indolyl) or the ring that does not contain a heteroatom (*e.g.*, 5-indolyl). In certain embodiments, the heteroaryl is substituted or unsubstituted, 5- or 6-membered, monocyclic heteroaryl, wherein 1, 2, 3, or 4 atoms in the heteroaryl ring system are independently oxygen, nitrogen, or sulfur. In certain embodiments, the heteroaryl is substituted or unsubstituted, 9- or 10-membered, bicyclic heteroaryl, wherein 1, 2, 3, or 4 atoms in the heteroaryl ring system are independently oxygen, nitrogen, or sulfur.

[0061] In some embodiments, a heteroaryl group is a 5-10 membered aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur ("5-10 membered heteroaryl"). In some embodiments, a heteroaryl group is a 5-8 membered aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur ("5-8 membered heteroaryl"). In some embodiments, a heteroaryl group is a 5-6 membered aromatic ring system having ring carbon atoms and 1–4 ring heteroatoms provided in the aromatic ring system, wherein each heteroatom is independently selected from nitrogen, oxygen, and sulfur ("5-6 membered heteroaryl"). In some embodiments, the 5-6 membered heteroaryl has 1–3 ring heteroatoms selected from nitrogen, oxygen, and sulfur. In some embodiments, the 5-6 membered heteroaryl has 1–2 ring heteroatoms selected from nitrogen, oxygen, and sulfur. In some embodiments, the 5-6 membered heteroaryl has 1 ring heteroatom selected from nitrogen, oxygen, and sulfur. Unless otherwise specified, each instance of a heteroaryl group is independently unsubstituted (an "unsubstituted heteroaryl") or substituted (a "substituted heteroaryl") with one or more substituents. In certain embodiments, the heteroaryl group is an unsubstituted 5-14 membered heteroaryl. In certain embodiments, the heteroaryl group is a substituted 5-14 membered heteroaryl.

[0062] Exemplary 5-membered heteroaryl groups containing 1 heteroatom include pyrrolyl, furanyl, and thiophenyl. Exemplary 5-membered heteroaryl groups containing 2 heteroatoms include imidazolyl, pyrazolyl, oxazolyl, isoxazolyl, thiazolyl, and isothiazolyl. Exemplary 5-membered heteroaryl groups containing 3 heteroatoms include triazolyl, oxadiazolyl, and thiadiazolyl. Exemplary 5-membered heteroaryl groups containing 4 heteroatoms include tetrazolyl. Exemplary 6-membered heteroaryl groups containing 1 heteroatom include pyridinyl. Exemplary 6-membered heteroaryl groups containing 2 heteroatoms include pyridazinyl, pyrimidinyl, and pyrazinyl. Exemplary 6-membered heteroaryl groups containing 3 or 4 heteroatoms include triazinyl and tetrazinyl, respectively. Exemplary 7-membered heteroaryl groups containing 1 heteroatom include azepinyl, oxepinyl, and thiepinyl. Exemplary 5,6-bicyclic heteroaryl groups include indolyl, isoindolyl, indazolyl, benzotriazolyl, benzothiophenyl, isobenzothiophenyl, benzofuranyl, benzoisofuranyl, benzimidazolyl, benzoxazolyl, benzisoxazolyl, benzoxadiazolyl, benzthiazolyl, benzisothiazolyl, benzthiadiazolyl, indolizinyl, and purinyl. Exemplary 6,6-bicyclic heteroaryl groups include naphthyridinyl, pteridinyl, quinolinyl, isoquinolinyl, cinnolinyl, quinoxalinyl, phthalazinyl, and quinazolinyl. Exemplary tricyclic heteroaryl groups include phenanthridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenothiazinyl, phenoxazinyl, and phenazinyl.

[0063] The term “unsaturated bond” refers to a double or triple bond.

[0064] The term “unsaturated” or “partially unsaturated” refers to a moiety that includes at least one double or triple bond.

[0065] The term “saturated” or “fully saturated” refers to a moiety that does not contain a double or triple bond, *e.g.*, the moiety only contains single bonds.

[0066] The term “acyl” refers to a group having the general formula $-C(=O)R^{X1}$, $-C(=O)OR^{X1}$, $-C(=O)-O-C(=O)R^{X1}$, $-C(=O)SR^{X1}$, $-C(=O)N(R^{X1})_2$, $-C(=S)R^{X1}$, $-C(=S)N(R^{X1})_2$, and $-C(=S)S(R^{X1})$, $-C(=NR^{X1})R^{X1}$, $-C(=NR^{X1})OR^{X1}$, $-C(=NR^{X1})SR^{X1}$, and $-C(=NR^{X1})N(R^{X1})_2$, wherein R^{X1} is hydrogen; halogen; substituted or unsubstituted hydroxyl; substituted or unsubstituted thiol; substituted or unsubstituted amino; substituted or unsubstituted acyl, cyclic or acyclic, substituted or unsubstituted, branched or unbranched aliphatic; cyclic or acyclic, substituted or unsubstituted, branched or unbranched heteroaliphatic; cyclic or acyclic, substituted or unsubstituted, branched or unbranched alkyl; cyclic or acyclic, substituted or unsubstituted, branched or unbranched alkenyl; substituted or unsubstituted alkynyl; substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, aliphaticoxy, heteroaliphaticoxy, alkyloxy, heteroalkyloxy, aryloxy, heteroaryloxy, aliphaticthioxy, heteroaliphaticthioxy, alkylthioxy, heteroalkylthioxy, arylthioxy, heteroarylthioxy, mono- or di- aliphaticamino, mono- or di- heteroaliphaticamino, mono- or di- alkylamino, mono- or di- heteroalkylamino, mono- or di-arylamino, or mono- or di-heteroarylamino; or two R^{X1} groups taken together form a 5- to 6-membered heterocyclic ring. Exemplary acyl groups include aldehydes (–CHO), carboxylic acids (–CO_2H), ketones, acyl halides, esters, amides, imines, carbonates, carbamates, and ureas. Acyl substituents include, but are not limited to, any of the substituents described herein, that result in the formation of a stable moiety (*e.g.*, aliphatic, alkyl, alkenyl, alkynyl, heteroaliphatic, heterocyclic, aryl, heteroaryl, acyl, oxo, imino, thiooxo, cyano, isocyano, amino, azido, nitro, hydroxyl, thiol, halo, aliphaticamino, heteroaliphaticamino, alkylamino, heteroalkylamino, arylamino, heteroarylamino, alkylaryl, arylalkyl, aliphaticoxy, heteroaliphaticoxy, alkyloxy, heteroalkyloxy, aryloxy, heteroaryloxy, aliphaticthioxy, heteroaliphaticthioxy, alkylthioxy, heteroalkylthioxy, arylthioxy, heteroarylthioxy, acyloxy, and the like, each of which may or may not be further substituted).

[0067] A “counterion” is a charged group associated with an oppositely charged group in order to maintain electronic neutrality.

[0068] As used herein, the term “salt” refers to any and all salts, and encompasses pharmaceutically acceptable salts. Salts include ionic compounds that result from the neutralization reaction of an acid and a base. A salt is composed of one or more cations (positively charged ions) and one or more anions (negative ions) so that the salt is electrically neutral (without a net charge). Salts of the compounds of the present disclosure include those derived from inorganic and organic acids and bases. Examples of acid addition salts are salts of an amino group formed with inorganic acids, such as hydrochloric acid, hydrobromic acid, phosphoric acid, sulfuric acid, and perchloric acid, or with organic acids, such as acetic acid, oxalic acid, maleic acid, tartaric acid, citric acid, succinic acid, or malonic acid or by using other methods known in the art such as ion exchange. Other salts include adipate, alginate, ascorbate, aspartate, benzenesulfonate, benzoate, bisulfate, borate, butyrate, camphorate, camphorsulfonate, citrate, cyclopentanepropionate, digluconate, dodecylsulfate, ethanesulfonate, formate, fumarate, glucoheptonate, glycerophosphate, gluconate, hemisulfate, heptanoate, hexanoate, hydroiodide, 2–hydroxy–ethanesulfonate, lactobionate, lactate, laurate, lauryl sulfate, malate, maleate, malonate, methanesulfonate, 2–naphthalenesulfonate, nicotinate, nitrate, oleate, oxalate, palmitate, pamoate, pectinate, persulfate, 3–phenylpropionate, phosphate, picrate, pivalate, propionate, stearate, succinate, sulfate, tartrate, thiocyanate, *p*-toluenesulfonate, undecanoate, valerate, hippurate, and the like. Salts derived from appropriate bases include alkali metal, alkaline earth metal, ammonium and $N^+(C_{1-4}\text{ alkyl})_4$ salts. Representative alkali or alkaline earth metal salts include sodium, lithium, potassium, calcium, magnesium, and the like. Further salts include ammonium, quaternary ammonium, and amine cations formed using counterions such as halide, hydroxide, carboxylate, sulfate, phosphate, nitrate, lower alkyl sulfonate, and aryl sulfonate.

[0069] As used herein the term “thermal treatment” refers to any method capable of generating heat to induce a chemical reaction or physical process; such methods include but are not limited to, supplying heat using hot-air convection furnaces, magnetic induction, microwave radiation, infrared radiation, near-infrared radiation, optionally combined with near-infrared dyes such as but not limited to, cyanines, porphyrine dyes, squaraine dyes, phtalocyanines, squarylium salts, diimonium salts, and dithiolene complexes.

[0070] In connection with the present disclosure, the term “additive manufacturing” refers to any process involving vat photopolymerization, material jetting, binder jetting, powder bed fusion, material extrusion, directed energy deposition, sheet lamination, extrusion, and/or layer casting. Vat photopolymerization techniques include stereolithography (SLA), Digital Light Processing (DLP), and Continuous Liquid Interface Production (CLIP).

[0071] As used herein, the term “Stereolithography” or “SLA” refers to a form of 3D printing technology used for creating models, prototypes, patterns, and production of parts in a layer-by-layer fashion using photopolymerization, a process by which light causes chains of molecules to link, forming polymers. Those polymers then make up the body of a three-dimensional solid.

[0072] As used herein, the term “Digital Light Processing” or “DLP” refers to an additive manufacturing process, also known as 3D printing and stereolithography, which takes a design created in a 3D modeling software and uses DLP technology to print a 3D object. DLP is a display device based on optical micro-electro-mechanical technology that uses a digital micromirror device. DLP may use a light source in printers to cure resins into solid 3D objects.

[0073] Use of the phrase “at least one instance” refers to 1, 2, 3, 4, or more instances, but also encompasses a range, *e.g.*, for example, from 1 to 4, from 1 to 3, from 1 to 2, from 2 to 4, from 2 to 3, or from 3 to 4 instances, inclusive.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

[0074] Provided herein are methods of preparing poly(meth)acrylimide materials and associated precursor polymers.

[0075] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation to form a solid layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer; and

(b) imidizing the precursor polymer to generate the poly(meth)acrylimide.

[0076] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation to form a solid layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

(b) imidizing at least a section of the solid layer of the precursor polymer to generate the poly(meth)acrylimide.

[0077] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation to form a layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

at the end of the irradiation, the reaction mixture has a percent conversion of at least 40%; and

(b) imidizing at least a section of the layer of the precursor polymer to generate the poly(meth)acrylimide.

[0078] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

at the start of the irradiation, a percent conversion of the reaction mixture is less than 10%;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 20%;

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

[0079] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

[0080] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising the steps of:

(a) irradiating a reaction mixture with radiation comprising actinic radiation to form a precursor polymer, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules, a near-infrared dye, and an initiator,

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer, and

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 2500 nm; and

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

[0081] In some embodiments, provided herein is a method of preparing a poly(meth)acrylimide, the method comprising:

irradiating a material comprising a precursor polymer and a near-infrared dye with radiation comprising actinic radiation to imidize at least a portion of the precursor polymer to generate the poly(meth)acrylimide,

wherein:

the precursor polymer comprises an optionally substituted polyacrylate, an optionally substituted polyacrylamide, an optionally substituted polyacrylonitrile, an optionally substituted polyacrylic acid, and/or any copolymer thereof, and

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 2500 nm.

[0082] In some embodiments, provided herein is a poly(meth)acrylimide prepared according to any method provided herein.

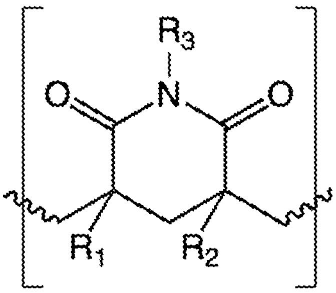
[0083] Compositions according to the disclosure for producing precursor polymers (*e.g.*, comprising one or more of poly(meth)acrylamide, poly(meth)acrylate, poly(meth)acrylonitrile) for poly(meth)acrylimide materials can include polymerizable mixtures (*e.g.*, reaction mixtures). The reaction mixtures or polymerizable mixtures may comprise a plurality of monomer molecules. In some embodiments, the plurality of monomer molecules comprises a plurality of monomer molecules each having the same chemical structure. In some embodiments, the plurality of monomer molecules comprises a plurality of monomer molecules each having the same chemical structure such that polymerizing the plurality of monomer molecules generates a homopolymer. In some embodiments, the plurality of monomer molecules comprises a plurality of monomer molecules having one or more chemical structures. In some embodiments, the plurality of monomer molecules comprises a plurality of monomer molecules having one or more chemical structures such that polymerizing the plurality of monomer molecules generates a copolymer. In some embodiments, the polymerizable mixtures may comprise at least one, or two or more, monomers, for example (meth)acrylic acid and (meth)acrylamide, optionally at least one polymerization initiator, and optionally a blowing agent for optional production of foam materials. These compositions can be polymerized to generate precursor polymers, which upon thermal treatment may result in poly(meth)acrylimide materials, via a cyclization reaction, herein termed imidization.

[0084] Polymers and oligomers can comprise a plurality of repeat units. In some embodiments, a polymer comprises eleven or more repeat units. In some embodiments, an oligomer comprises two to ten repeat units. In some embodiments, a polymer is a homopolymer. In some embodiments, a polymer is a copolymer. In some embodiments, a polymer comprises a weight average molecular weight of at least 1,000 g/mol. In some embodiments, a polymer comprises a molecular weight of at least 2,000 g/mol. In some embodiments, a polymer comprises a molecular weight of at least 5,000 g/mol. In some embodiments, a polymer comprises a molecular weight of at least 10,000 g/mol. In some embodiments, a polymer comprises a molecular weight of at least 20,000 g/mol. In some embodiments, a polymer comprises a molecular weight of 1,000 g/mol to 5×10^6 g/mol. In some embodiments, a polymer comprises a weight average molecular weight of 2,000 g/mol to 5×10^6 g/mol. In some embodiments, a polymer comprises a molecular weight of 5,000 g/mol to 5×10^6 g/mol. In some embodiments, a polymer comprises a molecular weight of

10,000 g/mol to 5 x 10^6 g/mol. In some embodiments, a polymer comprises a molecular weight of 20,000 g/mol to 5 x 10^6 g/mol. The weight average molecular weight of a polymer can be determined via gel permeation chromatography.

[0085] The formulation “poly(meth)acrylimide” as used herein describes both polymethacrylimides and polyacrylimides. In some embodiments, the formulation “(meth)acrylimide” as used herein describes both methacrylimides and acrylimides. In some embodiments, a poly(meth)acrylimide comprises a polymethacrylimide and/or a polyacrylimide. In some embodiments, a poly(meth)acrylimide is a polymethacrylimide. In some embodiments a poly(meth)acrylimide is a polyacrylimide. In some embodiments, the poly(meth)acrylimide is optionally substituted.

[0086] The poly(meth)acrylimide materials after thermal imidization may contain the repeat units according to formula (I):



wherein:

R_1 and R_2 are the same or different and are each a hydrogen (acrylate) or methyl group (methacrylate),

R_3 is hydrogen, optionally substituted acyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted heteroalkenyl, optionally substituted heteroalkynyl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted aryl, optionally substituted heteroaryl, or a nitrogen protecting group.

[0087] In some embodiments, in at least one repeat unit, R_1 and R_2 are each methyl. In some embodiments, in at least one repeat unit, R_1 and R_2 are each hydrogen. In some embodiments, in at least one repeat unit, one of R_1 and R_2 is hydrogen and the other is methyl. In some embodiments, in at least one repeat unit, R_1 is hydrogen and R_2 is methyl. In some embodiments, in at least one repeat unit, R_1 is methyl and R_2 is hydrogen.

[0088] In some embodiments, R_3 is a hydrogen or optionally substituted alkyl, or optionally substituted aryl having up to 36 carbon atoms, or optionally substituted aliphatic, or optionally substituted heteroaliphatic, or optionally substituted aryl, or optionally substituted heteroaryl (and possibly even also optionally substituted carbocyclyl and optionally substituted heterocyclyl), which may additionally contain oxygen, nitrogen, sulphur and/or phosphorous atoms in the form of typical organic functionalities, such as for example, an ether, alcohol, acid, ester, amide, imide, phosphonic acid, phosphonic ester, phosphoric acid, phosphoric ester, phosphinic acid, phosphinic ester, sulphonic acid, sulphonic ester, sulphinic acid and/or sulphinic ester function, silicon, aluminium and boron atoms and/or halogens, such as fluorine, chlorine, bromine and/or iodine.

[0089] In some embodiments, in at least one repeat unit, R_3 is hydrogen, optionally substituted alkyl, or a nitrogen protecting group. In some embodiments, in at least one repeat unit, R_3 is hydrogen or a nitrogen protecting group. In some embodiments, in at least one repeat unit, R_3 is hydrogen. In some embodiments, in at least one repeat unit, R_3 is a nitrogen protecting group.

[0090] In some embodiments, in at least one repeat unit, R_3 is optionally substituted acyl.

[0091] In some embodiments, in at least one repeat unit, R_3 is hydrogen or optionally substituted alkyl. In some embodiments, in at least one repeat unit, R_3 is hydrogen or optionally substituted C_1-C_{36} alkyl. In some embodiments, in at least one repeat unit, R_3 is hydrogen or optionally substituted C_1-C_{20} alkyl. In some embodiments, in at least one repeat unit, R_3 is hydrogen or optionally substituted C_1-C_8 alkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted alkyl, optionally substituted alkenyl, or optionally substituted alkynyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted alkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{36} alkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{20} alkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_8 alkyl. The following may be mentioned as examples of R3, without being restricted to thereto: methyl, ethyl, propyl, 2-propyl, butyl, tert-butyl, hexyl, ethylhexyl, octyl, dodecyl, octadecyl. In some embodiments, in at least one repeat unit, R_3 is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, secbutyl, isobutyl, or t-butyl optionally substituted with hydroxy or alkoxy. In some embodiments, in at least one repeat unit, R_3 is methyl, ethyl, n-propyl, isopropyl, n-butyl, secbutyl, isobutyl, or t-butyl. In some embodiments, R_3 is hydrogen, methyl, 2-hydroxyethyl, or isopropyl. In some embodiments, R_3 is methyl. In some embodiments, R_3 is 2-hydroxyethyl. In some embodiments, R_3 is isopropyl.

[0092] In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{36} alkenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{20} alkenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_8

alkenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{36} alkynyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{20} alkynyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_8 alkynyl.

[0093] In some embodiments, in at least one repeat unit, R_3 is optionally substituted heteroalkyl, optionally substituted heteroalkenyl, or optionally substituted heteroalkynyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted heteroalkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{36} heteroalkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{20} heteroalkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_8 heteroalkyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{36} heteroalkenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{20} heteroalkenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_8 heteroalkenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{36} heteroalkynyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_{20} heteroalkynyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_1-C_8 heteroalkynyl.

[0094] In some embodiments, in at least one repeat unit, R_3 is optionally substituted carbocyclyl or optionally substituted heterocyclyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted carbocyclyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_3-C_8 carbocyclyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_5-C_6 carbocyclyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted heterocyclyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted 3- to 8-membered heterocyclyl.

[0095] In some embodiments, in at least one repeat unit, R_3 is optionally substituted aryl or optionally substituted heteroaryl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted aryl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted C_6-C_{10} aryl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted phenyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted heteroaryl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted 5- to 10-membered heterocyclyl. In some embodiments, in at least one repeat unit, R_3 is optionally substituted 5- to 6-membered heterocyclyl.

[0096] In some embodiments, a monomer or co-monomer is a molecule capable of homopolymerizing and/or copolymerizing by radical addition and being incorporated into a growing polymer chain. In some embodiments, a monomer or co-monomer provided herein is optionally substituted. Such comonomers may be, but not restricted to, acrylic acid or methacrylic acid, esters of acrylic or methacrylic acid, N-substituted (meth)acrylamides, vinyl ethers, styrenes, acrylamides, maleimides, vinyl esters, vinylpyrrolidone, vinylic cyclic structures such as, but not limited to, vinyl acetal, vinyl ethers, spiro-ortho-carbonates, spiro-ortho-esters, vinyl sulfones, allilyc sulfides, vinyl oxirane, ketene acetals, and thionolactones.

[0097] In some embodiments, an acrylate monomer comprises a vinylic acid or ester moiety. In some embodiments, an acrylate monomer is optionally substituted. In some embodiments, an acrylate monomer is an unsubstituted acrylate monomer. In some embodiments, an acrylate monomer is a substituted acrylate monomer. In some embodiments, an acrylate monomer is an acrylic ester monomer optionally substituted at the ester position, a methacrylic ester monomer optionally substituted at the ester position, an acrylic acid monomer, a methacrylic acid monomer, a salt of an acrylic acid monomer, or a salt of a methacrylic acid monomer. As used herein, the term (meth)acrylate comprehends both acrylate monomers that are not substituted at the vinylic position to form methacrylates and methacrylate monomers. In other words, (meth)acrylates can include unsubstituted acrylates, acrylates substituted at the vinylic position to form methacrylates, acrylates that are substituted at the ester position but not substituted at the vinylic position, and acrylates that are substituted at both the vinylic position and ester position.

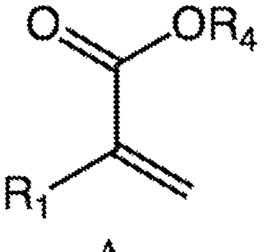
[0098] Examples of acrylate monomers include, but are not limited to, acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl acrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isobornyl methacrylate, isobornyl acrylate, glycidyl acrylate, glycidyl methacrylate, dicyclopentanyl acrylate, and dicyclopentanyl metahcrylate.

[0099] As used herein, the term “acrylic-containing group” or “methacrylate-containing group” refers to a compound that has a polymerizable acrylate or methacrylate group.

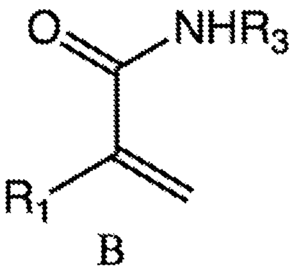
[00100] In some embodiments, an acrylamide monomer comprises a vinylic amide moiety. In some embodiments, an acrylamide monomer is optionally substituted. In some embodiments, an acrylamide monomer is an unsubstituted acrylamide monomer. In some embodiments, an acrylamide monomer is a substituted acrylamide monomer. In some embodiments, an acrylamide monomer is an acrylamide monomer optionally substituted at the vinylic position or an acrylamide monomer optionally substituted at the amide nitrogen atom. As used herein, the term (meth)acrylamide comprehends both acrylamide monomers that are not substituted at the vinylic position to form methacrylamides and methacrylamide monomers. In other words, (meth)acrylamides can include unsubstituted acrylamides, acrylamides substituted at the vinylic position to form methacrylamides, acrylamides that are substituted at the amide nitrogen atom but not substituted at the vinylic position, and acrylamides that are substituted at both the vinylic position and the amide nitrogen atom. Examples of acrylamide monomers include, but are not limited to, acrylamide, methacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-butylacrylamide, N-[3-(dimethylamino)propyl]acrylamide, 4-acryloylmorpholine, N-[2-(dimethylamino)ethyl]acrylamide, N-[2-(diethylamino)ethyl]acrylamide, diacetone acrylamide, N-(2-hydroxyethyl)acrylamide, N-isopropylacrylamide, N-propylacrylamide, N-(2-amino-2-oxoethyl)acrylamide, N-tert-butylacrylamide, N-(hydroxymethyl)acrylamide, and 3-acryloyl-2-oxazolidinone.

[00101] In some embodiments, an acrylonitrile monomer comprises a vinylic nitrile moiety. In some embodiments, an acrylonitrile monomer is optionally substituted. In some embodiments, an acrylonitrile monomer is an unsubstituted acrylonitrile monomer. In some embodiments, an acrylonitrile monomer is a substituted acrylonitrile monomer. In some embodiments, an acrylonitrile monomer is an acrylonitrile monomer optionally substituted at the vinylic position. As used herein, the term (meth)acrylonitrile comprehends both acrylonitrile monomers and methacrylonitrile monomers.

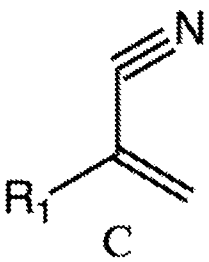
[00102] Methods for forming the structural moieties displayed in formula (I) in the polymer may involve neighboring repeat units able to undergo a cyclization reaction. Such repeat units may be introduced in the polymer by polymerizing monomers according to one or more of formulae (A), (B), or (C):



A



B



C

wherein:

each instance of R_1 is independently a hydrogen or methyl group,

R_3 and R_4 are each independently hydrogen, optionally substituted acyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted heteroalkenyl, optionally substituted heteroalkynyl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted aryl, optionally substituted heteroaryl, a nitrogen protecting group when attached to a nitrogen atom, or an oxygen protecting group when attached to an oxygen atom.

[00103] In some embodiments, at least one instance of R_1 is methyl. In some embodiments, at least one instance of R_1 is hydrogen. In some embodiments, each instance of R_1 is methyl. In some embodiments, each instance of R_1 is hydrogen.

[00104] In some embodiments, R_3 and R_4 are the same or different and are each a hydrogen or optionally substituted substituted alkyl or optionally substituted aryl having up to 36 carbon atoms, which may additionally contain oxygen, nitrogen, sulphur and/or phosphorous atoms in the form of typical organic functionalities, such as for example, an ether, alcohol, acid, ester, amide, imide, phosphonic acid, phosphonic ester, phosphoric acid, phosphoric ester, phosphinic acid, phosphinic ester, sulphonic acid, sulphonic ester, sulphinic acid and/or sulphinic ester function, silicon, aluminium and/or boron atoms or halogens, such as fluorine, chlorine, bromine and/or iodine. The following may be mentioned as examples of R3, without being restricted to thereto: methyl, ethyl, propyl, 2-propyl, butyl, tert-butyl, hexyl, ethylhexyl, octyl, dodecyl, octadecyl.

[00105] In some embodiments, R_3 is hydrogen, optionally substituted acyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted heteroalkenyl, optionally substituted heteroalkynyl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted aryl, optionally substituted heteroaryl, or a nitrogen protecting group when attached to a nitrogen atom.

[00106] In some embodiments, R_3 is hydrogen, optionally substituted alkyl, or a nitrogen protecting group. In some embodiments, R_3 is hydrogen or a nitrogen protecting group. In some embodiments, R_3 is hydrogen. In some embodiments, R_3 is a nitrogen protecting group.

[00107] In some embodiments, R_3 is optionally substituted acyl.

[00108] In some embodiments, R_3 is hydrogen or optionally substituted alkyl. In some embodiments, R_3 is hydrogen or optionally substituted C_1-C_{36} alkyl. In some embodiments, R_3 is hydrogen or optionally substituted C_1-C_{20} alkyl. In some embodiments, R_3 is hydrogen or optionally substituted C_1-C_8 alkyl. In some embodiments, R_3 is optionally substituted alkyl, optionally substituted alkenyl, or optionally substituted alkynyl. In some embodiments, R_3 is optionally substituted alkyl. In some embodiments, R_3 is optionally substituted C_1-C_{36} alkyl. In some embodiments, R_3 is optionally substituted C_1-C_{20} alkyl. In some embodiments,

R_3 is optionally substituted C_1-C_8 alkyl. In some embodiments, R_3 is methyl, ethyl, propyl, 2-propyl, butyl, tert-butyl, hexyl, ethylhexyl, octyl, dodecyl, octadecyl. In some embodiments, R_3 is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, secbutyl, isobutyl, or t-butyl optionally substituted with hydroxy or alkoxy. In some embodiments, R_3 is methyl, ethyl, n-propyl, isopropyl, n-butyl, secbutyl, isobutyl, or t-butyl. In some embodiments, R_3 is hydrogen, methyl, 2-hydroxyethyl, or isopropyl. In some embodiments, R_3 is methyl. In some embodiments, R_3 is 2-hydroxyethyl. In some embodiments, R_3 is isopropyl.

[00109] In some embodiments, R_3 is optionally substituted C_1-C_{36} alkenyl. In some embodiments, R_3 is optionally substituted C_1-C_{20} alkenyl. In some embodiments, R_3 is optionally substituted C_1-C_8 alkenyl. In some embodiments, R_3 is optionally substituted C_1-C_{36} alkynyl. In some embodiments, R_3 is optionally substituted C_1-C_{20} alkynyl. In some embodiments, R_3 is optionally substituted C_1-C_8 alkynyl.

[00110] In some embodiments, R_3 is optionally substituted heteroalkyl, optionally substituted heteroalkenyl, or optionally substituted heteroalkynyl. In some embodiments, R_3 is optionally substituted heteroalkyl. In some embodiments, R_3 is optionally substituted C_1-C_{36} heteroalkyl. In some embodiments, R_3 is optionally substituted C_1-C_{20} heteroalkyl. In some embodiments, R_3 is optionally substituted C_1-C_8 heteroalkyl. In some embodiments, R_3 is optionally substituted C_1-C_{36} heteroalkenyl. In some embodiments, R_3 is optionally substituted C_1-C_{20} heteroalkenyl. In some embodiments, R_3 is optionally substituted C_1-C_8 heteroalkenyl. In some embodiments, R_3 is optionally substituted C_1-C_{36} heteroalkynyl. In some embodiments, R_3 is optionally substituted C_1-C_{20} heteroalkynyl. In some embodiments, R_3 is optionally substituted C_1-C_8 heteroalkynyl.

[00111] In some embodiments, R_3 is optionally substituted carbocyclyl or optionally substituted heterocyclyl. In some embodiments, R_3 is optionally substituted carbocyclyl. In some embodiments, R_3 is optionally substituted C_3-C_8 carbocyclyl. In some embodiments, R_3 is optionally substituted C_5-C_6 carbocyclyl. In some embodiments, R_3 is optionally substituted heterocyclyl. In some embodiments, R_3 is optionally substituted 3- to 8-membered heterocyclyl.

[00112] In some embodiments, R_3 is optionally substituted aryl or optionally substituted heteroaryl. In some embodiments, R_3 is optionally substituted aryl. In some embodiments, R_3 is optionally substituted C_6-C_{10} aryl. In some embodiments, R_3 is optionally substituted phenyl. In some embodiments, R_3 is optionally substituted heteroaryl. In some embodiments, R_3 is optionally substituted 5- to 10-membered heterocyclyl. In some embodiments, R_3 is optionally substituted 5- to 6-membered heterocyclyl.

[00113] In some embodiments, R_4 is hydrogen, optionally substituted acyl, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted heteroalkyl, optionally substituted heteroalkenyl, optionally substituted heteroalkynyl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted aryl, optionally substituted heteroaryl, or an oxygen protecting group when attached to an oxygen atom.

[00114] In some embodiments, R_4 is hydrogen, optionally substituted alkyl, or an oxygen protecting group. In some embodiments, R_4 is hydrogen or an oxygen protecting group. In some embodiments, R_4 is hydrogen. In some embodiments, R_4 is an oxygen protecting group.

[00115] In some embodiments, R_4 is optionally substituted acyl.

[00116] In some embodiments, R_4 is hydrogen or optionally substituted alkyl. In some embodiments, R_4 is hydrogen or optionally substituted C_1-C_{36} alkyl. In some embodiments, R_4 is hydrogen or optionally substituted C_1-C_{20} alkyl. In some embodiments, R_4 is hydrogen or optionally substituted C_1-C_8 alkyl. In some embodiments, R_4 is optionally substituted alkyl, optionally substituted alkenyl, or optionally substituted alkynyl. In some embodiments, R_4 is optionally substituted alkyl. In some embodiments, R_4 is optionally substituted C_1-C_{36} alkyl. In some embodiments, R_4 is optionally substituted C_1-C_{20} alkyl. In some embodiments, R_4 is optionally substituted C_1-C_8 alkyl. In some embodiments, R_4 is methyl, ethyl, propyl, 2-propyl, butyl, tert-butyl, hexyl, ethylhexyl, octyl, dodecyl, octadecyl. In some embodiments, R_4 is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, secbutyl, isobutyl, or t-butyl optionally substituted with hydroxy or alkoxy. In some embodiments, R_4 is methyl, ethyl, n-propyl, isopropyl, n-butyl, secbutyl, isobutyl, or t-butyl. In some embodiments, R_4 is hydrogen, methyl, 2-hydroxyethyl, or isopropyl. In some embodiments, R_4 is methyl. In some embodiments, R_4 is 2-hydroxyethyl. In some embodiments, R_4 is isopropyl.

[00117] In some embodiments, R_4 is optionally substituted C_1-C_{36} alkenyl. In some embodiments, R_4 is optionally substituted C_1-C_{20} alkenyl. In some embodiments, R_4 is optionally substituted C_1-C_8 alkenyl. In some embodiments, R_4 is optionally substituted C_1-C_{36} alkynyl. In some embodiments, R_4 is optionally substituted C_1-C_{20} alkynyl. In some embodiments, R_4 is optionally substituted C_1-C_8 alkynyl.

[00118] In some embodiments, R_4 is optionally substituted heteroalkyl, optionally substituted heteroalkenyl, or optionally substituted heteroalkynyl. In some embodiments, R_4 is optionally substituted heteroalkyl. In some embodiments, R_4 is optionally substituted C_1-C_{36} heteroalkyl. In some embodiments, R_4 is optionally substituted C_1-C_{20} heteroalkyl. In some embodiments, R_4 is optionally substituted C_1-C_8 heteroalkyl. In some embodiments, R_4 is optionally substituted C_1-C_{36} heteroalkenyl. In some embodiments, R_4 is optionally substituted C_1-C_{20} heteroalkenyl. In some embodiments, R_4 is optionally substituted C_1-C_8 heteroalkenyl. In some embodiments, R_4 is optionally substituted C_1-C_{36} heteroalkynyl. In some embodiments, R_4 is optionally substituted C_1-C_{20} heteroalkynyl. In some embodiments, R_4 is optionally substituted C_1-C_8 heteroalkynyl.

[00119] In some embodiments, R_4 is optionally substituted carbocyclyl or optionally substituted heterocyclyl. In some embodiments, R_4 is optionally substituted carbocyclyl. In some embodiments, R_4 is optionally substituted C_3-C_8 carbocyclyl. In some embodiments, R_4 is optionally substituted C_5-C_6 carbocyclyl. In some embodiments, R_4 is optionally substituted heterocyclyl. In some embodiments, R_4 is optionally substituted 3- to 8-membered heterocyclyl.

[00120] In some embodiments, R_4 is optionally substituted aryl or optionally substituted heteroaryl. In some embodiments, R_4 is optionally substituted aryl. In some embodiments, R_4 is optionally substituted C_6-C_{10} aryl. In some embodiments, R_4 is optionally substituted phenyl. In some embodiments, R_4 is optionally substituted heteroaryl. In some embodiments, R_4 is optionally substituted 5- to 10-membered heterocyclyl. In some embodiments, R_4 is optionally substituted 5- to 6-membered heterocyclyl.

[00121] In some embodiments, Monomer A represents (meth)acrylic acid and/or (meth)acrylate esters, monomer B represents (meth)acrylamides, monomer C represents (meth)acrylonitriles. Monomers may be used in variable molar ratios. In some embodiments, to facilitate imidization, monomer A is combined with monomer B or C, or a combination of both B and C. In some embodiments, monomer B is used alone, or in combination with monomer A. In some embodiments, monomer C is combined with monomer A.

[00122] In some embodiments, the first step in producing resins is the production of monomer mixtures containing a (meth)acrylic acid or (meth)acrylic ester, or combination thereof, with a (meth)acrylamide or (meth)acrylonitrile, or combination thereof. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylic ester monomer, an optionally substituted methacrylic ester monomer, an acrylic acid monomer, a methacrylic acid monomer, an optionally substituted acrylamide monomer, an optionally substituted methacrylamide monomer, an acrylonitrile monomer, and/or a methacrylonitrile monomer. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylonitrile and an optionally substituted acrylic acid. In some embodiments, the plurality of monomer molecules comprises acrylonitrile and acrylic acid. In some embodiments, the plurality of monomer molecules comprises methacrylonitrile and acrylic acid. In some embodiments, the plurality of monomer molecules comprises acrylonitrile and methacrylic acid. In some embodiments, the plurality of monomer molecules comprises methacrylonitrile and methacrylic acid. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylonitrile and an optionally substituted acrylic ester. In some embodiments, the plurality of monomer molecules comprises acrylonitrile and an optionally substituted acrylic ester. In some embodiments, the plurality of monomer molecules comprises methacrylonitrile and an optionally substituted acrylic ester.

[00123] It was surprisingly found that completely substituting the (meth)acrylonitrile monomer with (meth)acrylamide may result in PMI materials, in particular foams, with improved thermomechanical properties, and/or may avoid the toxicological concerns related to (meth)acrylonitrile. In addition, replacing (meth)acrylonitrile with (meth)acrylamide may reduce toxicological concerns. Accordingly, in some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylamide monomer, an optionally substituted acrylic ester monomer, and/or an optionally substituted acrylic acid monomer. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylic ester monomer, an optionally substituted methacrylic ester monomer, an acrylic acid monomer, a methacrylic acid monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted methacrylamide monomer. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylate monomer and an optionally substituted acrylamide monomer. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylamide and an optionally substituted acrylic ester. In some embodiments, the plurality of monomer molecules comprises an optionally substituted acrylamide and an optionally substituted acrylic acid. In some embodiments, the plurality of monomer molecules comprises methacrylic acid and methacrylamide.

[00124] In some embodiments, the molar ratio of an optionally substituted acrylate monomer to an optionally substituted acrylamide monomer is between 10:90 and 90:10. In some embodiments, the molar ratio of an optionally substituted acrylate monomer to an optionally substituted acrylamide monomer is between 20:80 and 80:20. In some embodiments, the molar ratio of an optionally substituted acrylate monomer to an optionally substituted acrylamide monomer is between 40:60 and 60:40. In some embodiments, the molar ratio of an optionally substituted acrylate monomer to an optionally substituted acrylamide monomer is between 45:55 and 55:45. In some embodiments, the molar ratio of an optionally substituted acrylate monomer to an optionally substituted acrylamide monomer is between 49:51 and 51:49. In one embodiment, the molar ratio of (meth)acrylic acid monomer to (meth)acrylamide as main constituents is between 20:80 and 80:20. In some embodiments, the molar ratio of (meth)acrylic acid monomer to (meth)acrylamide as main constituents is between 40:60 and 60:40. In some embodiments, the molar ratio of (meth)acrylic acid monomer to (meth)acrylamide as main constituents is between 51:49 to 49:51. In one embodiment, the molar ratio of (meth)acrylic ester monomer to (meth)acrylamide as main constituents is between 20:80 and 80:20. In some embodiments, the molar ratio of (meth)acrylic ester monomer to (meth)acrylamide as main constituents is between 40:60 and 60:40. In some embodiments, the molar ratio of (meth)acrylic ester monomer to (meth)acrylamide as main constituents is between 51:49 to 49:51.

[00125] Additional suitable comonomers may be used be used such as esters of acrylic or methacrylic acid, N-substituted (meth)acrylamides vinyl ethers, styrenes, acrylamides, maleimides, vinyl esters, vinylpyrrolidone, vinylic cyclic structures such as but not limited to vinyl acetal, vinyl ethers, spiro-ortho-carbonates, spiro-ortho-esters, vinyl sulfones, allylic sulfides, vinyl oxirane, ketene acetals, thionolactones. These comonomers are intended as examples and are not limiting. In some embodiments, the proportion of comonomers does not amount to more than 50% by weight of the two main constituents. In some embodiments, the proportion of comonomers does not amount to more than 40% by weight of the two main constituents. In some embodiments, the proportion of comonomers does not amount to more than 35% by weight of the two main constituents. In some embodiments, the proportion of comonomers does not amount to more than 20% by weight of the two main constituents. In some embodiments, the proportion of comonomers does not amount to more than 10% by weight of the two main constituents. In some embodiments, the additional comonomers comprise less than 50 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise less than 35 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise less than 20 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise less than 10 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise less than 5 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 1 mol% to 50 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 1 mol% to 35 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 1 mol% to 20 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 1 mol% to 10 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 1 mol% to 5 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 5 mol% to 50 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 5 mol% to 35 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 5 mol% to 20 mol% of the reaction mixture. In some embodiments, the additional comonomers comprise 5 mol% to 10 mol% of the reaction mixture.

[00126] In some embodiments, the reaction mixture further comprises one or more cross-linkers. In some embodiments, a cross-linker links one polymer chain to at least one other polymer chain, *e.g.*, via one or more covalent bonds. In some embodiments, a cross-linker comprises two or more functional groups that may react to link one polymer chain to at least one other polymer chain. In some embodiments, a cross-linker is a comonomer comprising two or more polymerizable moieties. In some embodiments, a cross-linker comprises two or more vinylic moieties. In some embodiments, a cross-linker comprises two or more acylate, acrylamide, and/or acrylonitrile moieties. The terms “cross-linker, “crosslinking monomer,” “crosslinking molecule,” and “crosslinking agent” are used interchangeably herein.

[00127] Small amounts of crosslinking unsaturated monomers can be used, having at least two 2 polymerizable functionalities in the molecule. In some embodiments, the cross-linker comprises at least two polymerizable functionalities in the molecule (*e.g.*, at least two vinylic groups). In some embodiments, the cross-liner comprises two, three, or four polymerizable functionalities in the molecule. In some embodiments, the cross-linker comprises the same polymerizable functionalities as the plurality of monomer molecules. In some embodiments, the cross-linker comprises two or more polymerizable functionalities selected from an optionally substituted acrylate, an optionally substituted acrylamide, and/or an optionally substituted acrylonitrile. In some embodiments, the cross-linker comprises two or more polymerizable functionalities selected from an optionally substituted acrylate or an optionally substituted acrylamide.

[00128] Examples of cross-linkers include, but are not limited to, butanediol di(meth)acrylate, triallylisocyanurate, triacrylate isocyanurates (IGM Photomer 4356), pentaerythritol triacrylate, ethylene glycol acrylate, ethylene glycol methacrylate, triethylene glycol diacrylate, and triethylene glycol dimethacrylate. Unsaturated polymerizable oligomers or polymers having at least two 2 polymerizable functionalities may be used, for example but not limited to aliphatic urethane diacrylate or dimethacrylate oligomer (IGM

Photomer 6024, Sartomer CN9009, CN1964, CN9039), polyester acrylate oligomer (Allnex Ebecryl 830). Ionic crosslinking agents composed of polyvalent metal ions bound to polymerizable units such as but not limited to (meth)acrylic acids, with preference given to magnesium (meth)acrylate or zinc (meth)acrylates may also be used. In some embodiments, the one or more cross-linkers comprise ethylene glycol dimethacrylate, CN9009, or Photomer 4356. In some embodiments, the one or more cross-linkers comprise N-methacryloylmethacrylamide or N-acryloylacrylamide.

[00129] In some embodiments, the amounts of crosslinking molecules used is 0 to 20% by weight. In some embodiments, the amounts of crosslinking molecules used is 0 to 10% by weight. In some embodiments, the amounts of crosslinking molecules used is 0.05% to 5.0% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 50% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 40% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 30% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 20% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 15% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 10% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0% to 5% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 50% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 40% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 30% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 20% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 15% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 10% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 0.5% to 5% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 50% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 40% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 30% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 20% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 15% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 10% by weight. In some embodiments, the reaction mixture comprises cross-linker in an amount of 1% to 5% by weight.

[00130] In some embodiments, the percent conversion is the percentage of reactant that has been converted to product. For example, in the context of polymerization, percent conversion is the percentage of monomers or co-monomers that have been converted to polymer.

[00131] In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 40%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 35%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 30%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 25%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 20%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 15%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 10%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 5%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 2%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of less than 1%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 1% to 10%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 5% to 15%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 10% to 20%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 15% to 25%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 20% to 30%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 25% to 35%. In some embodiments, at the start of the irradiation, the reaction mixture has a percent conversion of 30% to 40%.

[00132] Further additional substances, which are different from the stated monomers, crosslinker, blowing agents, solvents, assisting polymers/oligomers (*e.g.*, homogenizers) or initiators can be admixed in the formulations (*e.g.*, dispersed therein). Suitable amounts of additives can be for instance between 0% and 20% wt. Additives can include, but are not limited to, antioxidants, dyes, thickeners, lubricants, fillers, UV absorbers, plasticizers, organic phosphorous compounds, release agents, flame retardants, graphite, graphene, fumed silica, glass beads or spheres, aluminum particles, and piezo electric-responsive fillers.

[00133] In some embodiments, the additive is present in an amount between 0 wt% and 50 wt%. In some embodiments, the additive is present in an amount between 0 wt% and 40 wt%. In some embodiments, the additive is present in an amount between 0 wt% and 30 wt%. In some embodiments, the additive is present in an amount between 0 wt% and 20 wt%. In some embodiments, the additive is present in an amount between 0 wt% and 15 wt%. In some embodiments, the additive is present in an amount between 0 wt% and 10 wt%. In some embodiments, the additive is present in an amount between 0 wt% and 5 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 50 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 40 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 30 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 20 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 15 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 10 wt%. In some embodiments, the additive is present in an amount between 0.5 wt% and 5 wt%. In some embodiments, the additive is present in an amount between 5 wt% and 10 wt%. In some embodiments, the additive is present in an amount between 10 wt% and 15 wt%. In some embodiments, the additive is present in an amount between 15 wt% and 20 wt%. In some embodiments, the additive is present in an amount between 20 wt% and 30 wt%. In some embodiments, the additive is present in an amount between 30 wt% and 40 wt%. In some embodiments, the additive is present in an amount between 40 wt% and 50 wt%.

[00134] In some embodiments, the reaction mixture further comprises one or more solvents. The composition may optionally contain a solvent. Some solvents may enhance the homogeneity of the mixture at ambient temperature. In some embodiments, suitable solvents include those which are capable of volatilization during subsequent processing steps and which do not negatively affect the monomer copolymerization. In some embodiments, suitable solvents include water, which is believed to not negatively affect the safety profile of the mixture. In some embodiments, the one or more solvents comprises a polar solvent. In some embodiments, the one or more solvents comprises a polar protic solvent. In some embodiments, the one or more solvents comprises a polar aprotic solvent. In some embodiments, the one or more solvents comprise water. In some embodiments, the one or more solvents comprises glycerol. In some embodiments, the one or more solvents comprises a non-polar solvent. In some embodiments, the one or more solvents comprises toluene, benzene, cyclohexane, heptane, hexane, or pentane. In some embodiments, the one or more solvents comprises toluene, cyclohexane, or heptane.

[00135] In some embodiments, the one or more solvents comprise 0% to 35% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 0.1% to 35% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 1% to 35% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 5% to 35% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 1% to 20% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 5% to 20% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 1% to 5% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 5% to 10% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 8% to 20% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 8% to 15% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 8% to 12% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 10% to 20% of the reaction mixture by weight. In some embodiments, the one or more solvents comprise 20% to 35% of the reaction mixture by weight.

[00136] In some embodiments, the reaction mixture further comprises one or more blowing agents. In some embodiments, the layer of the precursor polymer further comprises one or more blowing agents. In some embodiments, a blowing agent comprises a compound which is capable of producing a cellular structure via a foaming process in a variety of materials that undergo hardening or phase transition. In some embodiments, the blowing agent is a substance that forms gas during the hardening or phase transition.

[00137] In some embodiments, the blowing agent causes foaming through a physical process. In some embodiments, the blowing agent is a volatile substance that forms gas when heated. In some embodiments, the blowing agent is added to a reaction mixture and/or a polymer (e.g., a precursor polymer) as an exogenous liquid or gaseous compound. In some embodiments, the one or more blowing agents is added to the reaction mixture as an exogenous liquid or gaseous compound. In some embodiments, the one or more blowing agents is added to the precursor polymer as an exogenous liquid or gaseous compound. In some embodiments, the blowing agent is an expandable bead (*e.g.*, a microsphere encapsulating a gas). In some embodiments, the blowing agent is added to a reaction mixture and/or a polymer (*e.g.*, a precursor polymer) as an expandable bead. In some embodiments, the one or more blowing agents is added to the reaction mixture as an expandable bead. In some embodiments, the one or more blowing agents is added to the precursor polymer as an expandable bead. Expandable beads include, but are not limited to, acrylic shells or micro-balloons (*e.g.*, Advancell Expandable Microspheres) and thermoplastic microspheres (*e.g.*, Expancel® microspheres).

[00138] In some embodiments, the blowing agent causes foaming through a chemical process. In some embodiments, the blowing agents causes foaming through a chemical reaction that produces a small molecule (*e.g.*, a volatile small molecule). In some embodiments, the blowing agent is generated during imidization of a precursor polymer described herein.

[00139] In some embodiments, a mixture for the copolymerisation further contains blowing agents which either decompose or vaporise at temperatures of about 120 °C to 250 °C, forming a gas phase in the process. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below the imidization temperature. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below 170 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below 160 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below 150 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below 150 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below 140 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature below 130 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above the imidization temperature. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 130 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 140 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 150 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 160 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 170 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 180 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 190 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 290 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 225 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above 250 °C. In some embodiments, the blowing agent decomposes or vaporizes at a temperature above glass transition temperature (T_g) of the precursor polymer.

[00140] In some embodiments, the one or more blowing agents comprise urea, monomethylurea, N,N’-dimethylurea, formamide, monomethylformamide, formic acid, water, an alcohol, a low molecular weight hydrocarbon, a low molecular weight halohydrocarbon, an organic carboxylic acid, liquid carbon dioxide, azodicarbonamide, and/or hydrazine. Examples of suitable blowing agents include, but are not limited to, the following compounds, or mixtures thereof: nitrogenous compounds, urea, monomethylurea or N,N'-dimethylurea, formamide or monomethylformamide. Further possible, nitrogen-free blowing agents include formic acid, water or mono hydric aliphatic alcohols particularly those of three to eight carbon atoms, for example propan-1-ol, propan-2-ol, butan-2-ol, tert-butanol and isobutanol. Organic carboxylic acids may include oxalic acid, maleic acid, citric acid, itaconic acid, hydroxyisobutyric acid, malonic acid. In some embodiments, the one or more blowing agents comprise urea. In some embodiments, the blowing agent is generated during imidization of the precursor polymer. In some embodiments, the blowing agent is generated during imidization of the precursor polymer by liberation of a small molecule byproduct of imidization. Blowing agents in the form of unsaturated copolymerisable monomers, such as tert-butyl(meth)acrylate, sec-butyl(meth)acrylate and isopropyl(meth)acrylate may also be used.

[00141] The blowing agents may be used in amounts of 0% to 20% by weight based on the monomers used and the desired density of the PMI material. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 20% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 15% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 10% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 5% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 20% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 15% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 10% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 5% by weight relative to the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 5% to 10% by weight of the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 10% to 15% by weight of the plurality of monomer molecules. In some embodiments, the reaction mixture comprises blowing agent in an amount of 15% to 20% by weight of the plurality of monomer molecules.

[00142] In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 80% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 60% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 40% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0% to 20% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 80% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 60% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 40% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 0.5% to 20% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 5% to 80% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 5% to 60% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 5% to 40% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 5% to 20% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 20% to 40% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 40% to 60% by volume. In some embodiments, the reaction mixture comprises blowing agent in an amount of 60% to 80% by volume.

[00143] In some embodiments, the reaction mixture is homogenous (*e.g.*, a uniform blend of its constituents, such as a uniform blend as determined by light scattering, *e.g.*, dynamic light scattering). In some embodiments, the reaction mixture is homogenous prior to the addition of an additive. In some embodiments, the reaction mixture is homogenous prior to the addition of a filler. In some embodiments, the reaction mixture is a single phase. In some embodiments, the reaction mixture does not include a precipitate or includes precipitates in a relatively small amount (e.g., less than or equal to 5 wt%, less than or equal to 2 wt%, less than or equal to 1 wt%, less than or equal to 0.5 wt%, less than or equal to 0.2 wt%, less than or equal to 0.1 wt%, and, e.g., greater than or equal to 0 wt%).The method of any one of the preceding claims, wherein the reaction mixture further comprises a homogenizer. In some embodiments, a homogenizer comprises an oligomer, polymer, or copolymer which helps in homogenizing the polymerization of the monomers, preventing phase separation during the polymerization reaction, and/or resulting in homogeneous materials.

[00144] The monomer compositions may include oligomeric and/or polymeric resins of suitable molecular weights to assist in the formation of PMI resins and foams. These include, for example, PMMA (polymethylmethacrylate) and/or PMMI (poly-N-methylmethacrylimide). Such polymers are believed to have good incorporability. In some embodiments, the syrup phase resulting from addition of PMMA can be realized by means of high molecular weight PMMA, which may be prepared by emulsion or solution polymerization. For example, the product Degalan BT 310 produced by Röhm may serve for this purpose. In some embodiments, the amount of dissolved PMMA is between 0.005 and 0.10 gram of PMMA per gram of monomer mixture which acts as a solvent.

[00145] In some embodiments, the reaction mixture further comprises an oligomer, polymer, or copolymer. In some embodiments, the reaction mixture further comprises one or more of PMMA, PMMI, Degalan BT 310, or Elvacite. In some embodiments, the reaction mixture further comprises a vinylic copolymer. In some embodiments, the reaction mixture further comprises a polyvinylbutyrate.

[00146] In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.001 g to 0.60 g per gram of monomer mixture. In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.001 g to 0.50 g per gram of monomer mixture. In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.001 g to 0.20 g per gram of monomer mixture. In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.005 g to 0.10 g per gram of monomer mixture. In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.005 g to 0.01 g per gram of monomer mixture. In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.01 g to 0.05 g per gram of monomer mixture. In some embodiments, the reaction mixture further comprises an oligomer or polymer in an amount of 0.05 g to 0.10 g per gram of monomer mixture.

[00147] In some embodiments, co-polymers of (meth)acrylamides and (meth)acrylic acid esters are used in combination with amine-generating blowing agents. Such species may react and turn the copolymer additives into P(M)I during the foaming process. It was surprisingly found that these homogenizers can, in some instances, prevent phase segregation during polymerization and/or assist and promote the foaming process. The number average molecular weight for these homogenizers can be up to 4×10^6 g/mol.

[00148] In some embodiments, an initiator is a substance or molecule that initiates a reaction, such as in polymerization. Typically, the initiator decomposes to form radical, anionic, or cationic species that serve as reactive sites for propagation of polymerization. In some embodiments, the initiator initiates free radical polymerization.

[00149] In some embodiments, the initiator is a photoinitiator. In some embodiments, a photoinitiator generates a reactive species when exposed to radiation (*e.g.*, actinic radiation, electromagnetic radiation, electron beam radiation). In some embodiments, the photoinitiator is a molecule that generates a free radical species when exposed to radiation. In some embodiments, the free radical species formed from the photoinitiator initiates polymerization of one or more monomers or comonomers.

[00150] In some embodiments, the initiator is a thermal intiator. In some embodiments, a thermal initiator generates a reactive species when exposed to thermal energy. In some embodiments, the thermal initiator generates a free radical species when exposed to radiation. In some embodiments, the free radical species formed from the thermal initiator initiates polymerization of one or more monomers or comonomers. In some embodiments, the thermal initiator is one or more of tert-amyl peroxybenzoate, 4,4-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobisisobutyronitrile, benzoyl peroxide, 2,2-bis(tert-butylperoxy)butane, 1,1-bis(tert-butylperoxy)cyclohexane, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, 2,5-bis(tert-butylperoxy)-2,5-dimethyl-3-hexyne, bis(1-(tert-butylperoxy)-1-methylethyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, tert-butyl hydroperoxide, tert-butyl peracetate, tert-butyl peroxide, tert-butyl peroxybenzoate, tert-butylperoxy isopropyl carbonate, cumene hydroperoxide, cyclohexanone peroxide, dicumyl peroxide, lauroyl peroxide, 2,4-pentanedione peroxide, peracetic acid, and/or potassium persulfate.

[00151] In some embodiments, the reaction mixture further comprises one or more photoinitiators. In some embodiments, the monomer compositions may include one or more photoinitiators. In some embodiments, the one or more photoinitiators comprise a benzoin ether, a benzil ketal, an α-dialkoxy-acetophenone, an α-hydroxy-alkylphenone, an α-amino alkylphenone, an acyl phosphine oxide, a benzophenone, a thioxanthone, and/or a metallocene. In some embodiments, the one or more photoinitiators comprise acetophenone, anisoin, anthraquinone, anthraquinone-2-sulfonic acid, benzene tricarbonylchromium, benzil, benzoin, benzoin ethyl ether, benzoin methyl ether, benzophenone, 1-hydroxycyclohexyl phenyl ketone, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4-benzoylbiphenyl, 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone, 4,4'-

bis(diethylamino)benzophenone, 4,4’-bis(dimethylamino)benzophenone, camphorquinone, 2-chlorothioxanthene-9-one, (cumene)cyclopentadienyl iron(ii) hexafluorophosphate, dibenzosuberenone, 2,2-diethoxyacetophenone, 4,4’-dihydroxybenzophenone, 2,2-dimethoxy-2-phenylacetophenone, 4-(dimethylamino)benzophenone, 4,4’-dimethylbenzil, 2,5-dimethylbenzophenone, 3,4-dimethylbenzophenone, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, 2-hydroxy-2-methylpropiophenone, 4’-ethoxyacetophenone, 2-ethylanthraquinone, ferrocene, 3’-hydroxyacetophenone, 4’-hydroxyacetophenone, 3-hydroxybenzophenone, 4-hydroxybenzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methylpropiophenone, 2-methylbenzophenone, 3-methylbenzophenone, methylbenzoylformate, 2-methyl-4’-(methylthio)-2-morpholinopropiophenone, phenanthrenequinone, 4’-phenoxyacetophenone, thioxanthene-9-one, triarylsulfonium hexafluoroantimonate salts, and/or triarylsulfonium hexafluorophosphate salts. In some embodiments, the one or more photoinitiators comprise bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, 2,4,6-trimethylbenzoylphenyl phosphinate, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, dipheny1(2,4,6-trimethylbenzoyl)phosphine oxide, alpha- hydroxycyclohexyl phenyl ketone, 2-hydroxy-1-(4-(4-(2-hydroxy-2-methy|propionyl)benzyl)phenyl-2-methy|propan-1-one,2-hydroxy-2-methyl-1- phenylpropanone,2-hydroxy-2-methyl-1-(4-isopropylphenyl)propanone,oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone, 2-hydroxy-2-methyl-1-(4-dodecylphenyl)propanone,2-hydroxy-2-methyl-1-[(2-hydroxyethoxy)pheny]]propanone,benzophenone, substituted benzophenones, and mixtures of any two or more thereof. In some embodiments, the one or more photoinitiators comprise diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, and combinations of two or more thereof. In some embodiments, the one or more photoinitiators comprise diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

[00152] In some embodiments, the initiator is a salt. In some embodiments, the initiator is an onium salt. In some embodiments, the initiator is an iodonium salt or a sulfonium salt. In some embodiments, the initiator is an iodonium salt or a sulfonium salt of formula $(R_A)_2I^+X_A{}^-$ or $(R_A)_3S^+X_A{}^-$; wherein each instance of R_A is independently optionally substituted $C_{6\text{-}10}$ aryl or optionally substituted $C_{1\text{-}10}$ alkyl; and $X_A{}^-$ is a counter ion. In some embodiments, the initiator is bis(2,4,6-trimethylpyridine)iodonium hexafluorophosphate, bis(4-tert-butylphenyl)iodonium hexafluorophosphate, bis(4-bromophenyl)iodonium trifluoromethanesulfonate, bis(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (3-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate, bis(4-tert-butylphenyl)iodonium tetrafluoroborate, bis(4-tert-butylphenyl)iodonium nonafluoro-1-butanesulfonate, bis(4-tert-butylphenyl)iodonium chloride, diphenyliodonium perchlorate, diphenyliodonium trifluoromethanesulfonate, diphenyliodonium chloride, diphenyliodonium bromide, diphenyliodonium-2-carboxylate monohydrate, 4-Isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate, (2-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (3-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (4-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (4-Nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate, Phenyl[3-(trifluoromethyl)phenyl]iodonium trifluoromethanesulfonate, [3-(trifluoromethyl)phenyl](2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, [4-(trifluoromethyl)phenyl](2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, bis(4-fluorophenyl)iodonium trifluoromethanesulfonate, diphenyliodonium hexafluorophosphate, [4-fluoro-3-(trifluoromethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, bis(pyridine)iodonium tetrafluoroborate, 4-biphenylyl(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate, (3,5-dichlorophenyl)(2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, (5-fluoro-2-nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, [(4-trifluoromethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, phenyl(2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, [4-(bromomethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, or diphenyliodonium nitrate.

[00153] In some embodiments, the reaction mixture further comprises a reducing agent. In some embodiments, the reducing agent is a phosphine-based reducing agent or an amine-based reducing agent. In some embodiments, the reducing agent is 4-(diphenylphosphino)benzoic acid, 2-diphenylphosphinobenzoic acid, bis(2-diphenylphosphinophenyl)-ether, triomethoxyphenylphosphine, DPBP bidentate phosphine, 4-dimethylaminophenyldiphenylphosphine, (R,R) dach phenyl trost, triphenylphosphine, ethyl 4-dimethylaminobenzoate, 4-(dimethylamino)phenylacetic acid, triphenylamine, N,N-dibutylaniline, N-Ethyl-N-isopropylaniline, or 3-(dimethylamino)benzyl alcohol.

[00154] In some embodiments, one or more materials (e.g., a reaction mixture, a precursor polymer) may be irradiated with actinic radiation. The actinic radiation may be capable of initiating chemical reactions by formation of radical or ionic species. In some embodiments, actinic radiation types may include electromagnetic radiation or particle radiation such as electrons.

[00155] In some embodiments, polymerization of the monomer formulations is carried out under photoinitiated conditions by the use of radiation (*e.g.*, actinic radiation), with the option of using additive manufacturing techniques. In some embodiments, the radiation comprises actinic radiation. In some embodiments, the actinic radiation comprises electromagnetic radiation. In some embodiments, the actinic radiation comprises UV, visible, and/or infrared electromagnetic radiation. In one embodiment, initiation includes short wavelength and long wavelength ultraviolet light irradiation. Suitable short wavelength ultraviolet light irradiation includes UV-C or UV-B irradiation. In one embodiment, the short wavelength ultraviolet light irradiation is UV-C light. Suitable longwave ultraviolet light irradiation includes UV-A irradiation. In one embodiment visible light is used.

[00156] In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength greater than 100 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength greater than 200 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength greater than 300 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength greater than 400 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength greater than 500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength greater than 750 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 100 nm to less than 1 mm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 100 nm to less than 0.5 mm.

[00157] In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 100 nm to less than 750 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 100 nm to less than 280 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 280 nm to less than 315 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 315 nm to less than 400 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 1000 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 750 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 450 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 440 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 430 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 420 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 410 nm.

[00158] In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm to less than 1 mm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm to less than 4500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm to less than 2500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm to less than 1500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm to less than 1000 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 1000 nm to less than 1500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 1500 nm to less than 2500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 2500 nm to less than 4500 nm. In some embodiments, the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 4500 nm to less than 1 mm.

[00159] In some embodiments, the actinic radiation does not comprise gamma radiation.

[00160] In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 0.1 mW /cm^2 to 10 W/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 0.1 mW/cm^2 to 5 W/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 0.1 mW/cm^2 to 2 W/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 0.1 mW/cm^2 to 1 W/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 1 mW/cm^2 to 100 mW/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 100 mW/cm^2 to 1 mW/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 1 W/cm^2 to 10 W/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 1 mW/cm^2 to 100 mW/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 1 mW/cm^2 to 50 mW/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 1 mW/cm^2 to 10 mW/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 20 mW/cm^2 to 60 mW/cm^2. In some embodiments, the actinic radiation comprises electromagnetic radiation having an irradiance of 30 mW/cm^2 to 45 mW/cm^2.

[00161] In some embodiments, the actinic radiation comprises electron beam radiation. Additionally, Electron Beam (EB) irradiation may be utilized to induce curing of the composition.

[00162] In some embodiments, the duration of the irradiation is up to 300 minutes. In some embodiments, the duration of the irradiation is up to 180 minutes. In some embodiments, the duration of the irradiation is up to 120 minutes. In some embodiments, the duration of the irradiation is up to 60 minutes. In some embodiments, the duration of the irradiation is up to 30 minutes. In some embodiments, the duration of the irradiation is up to 20 minutes. In some embodiments, the duration of the irradiation is up to 15 minutes. In some embodiments, the duration of the irradiation is up to 10 minutes. In some embodiments, the duration of the irradiation is up to 5 minutes. In some embodiments, the duration of the irradiation is up to 2 minutes. In some embodiments, the duration of the irradiation is up to 1 minute. In some embodiments, the duration of the irradiation is up to 45 seconds. In some embodiments, the duration of the irradiation is up to 30 seconds. In some embodiments, the duration of the irradiation is up to 20 seconds. In some embodiments, the duration of the irradiation is up to 10 seconds. In some embodiments, the duration of the irradiation is up to 5 seconds. In some embodiments, the duration of the irradiation is up to 2 seconds. In some embodiments, the duration of the irradiation is up to 1 second. In some embodiments, the duration of the irradiation is up to 0.5 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 300 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 180 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 120 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 60 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 30 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 20 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 15 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 10 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 5 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 2 minutes. In some embodiments, the duration of the irradiation is 0.1 second to 1 minute. In some embodiments, the duration of the irradiation is 0.1 second to 45 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 30 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 20 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 10 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 5 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 2 seconds. In some embodiments, the duration of the irradiation is 0.1 second to 1 second. In some embodiments, the duration of the irradiation is 0.1 second to 0.5 seconds. In some embodiments, the duration of the irradiation is 0.5 second to 2 seconds. In some embodiments, the duration of the irradiation is 2 seconds to 5 seconds. In some embodiments, the duration of the irradiation is 5 seconds to 10 seconds. In some embodiments, the duration of the irradiation is 10 seconds to 20 seconds. In some embodiments, the duration of the irradiation is 20 seconds to 30 seconds. In some embodiments, the duration of the irradiation is 30 seconds to 2 minutes. In some embodiments, the duration of the irradiation is 2 minutes to 5 minutes. In some embodiments, the duration of the irradiation is 5 minutes to 10 minutes. In some embodiments, the duration of the irradiation is 10 minutes to 30 minutes. In some embodiments, the duration of the irradiation is 30 minutes to 60 minutes. In some embodiments, the duration of the irradiation is 60 minutes to 120 minutes. In some embodiments, the duration of the irradiation is 120 minutes to 180 minutes. In some embodiments, the duration of the irradiation is 180 minutes to 300 minutes.

[00163] In some embodiments, the duration of the irradiation is adjust based on the amount of the layer of the precursor polymer. In some embodiments, the duration of the irradiation is adjust based on the thickness of the layer of the precursor polymer.

[00164] In some embodiments, each side or face of a precursor polymer layer described herein is irradiated. In some embodiments, each side or face of a precursor polymer layer described herein is irradiated for a similar duration of time. In some embodiments, each side or face of a precursor polymer layer described herein is irradiated prior to imidization. In some embodiments, each side or face of a precursor polymer layer described herein is irradiated for a similar duration of time prior to imidization.

[00165] In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 100 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 90 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 80 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 70 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 60 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 50 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 40 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 35 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 30 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature less than 25 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 100 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 90 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 80 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 70 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 60 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 50 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 10 °C to 40 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 100 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 90 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 80 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 70 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 60 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 50 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 40 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 15 °C to 30 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 20 °C to 50 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 20 °C to 40 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 20 °C to 30 °C. In some embodiments, the irradiation of a reaction mixture is performed at a temperature of 20 °C to 25 °C.

[00166] In some embodiments, at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 25%. In some embodiments, at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 20%. In some embodiments, at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 15%. In some embodiments, at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 10%. In some embodiments, at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 5%. In some embodiments, the liquid comprises a solvent. In some embodiments, the liquid comprises unreacted monomer.

[00167] In some embodiments, a method is provided for preparing a 3D article using any of the compositions described in any embodiment herein. The method may include applying successive layers of one or more of the compositions described herein in any embodiment to fabricate a 3D article and/or irradiating the successive layers with UV irradiation.

[00168] Applying the composition to obtain the three-dimensional article may include depositing the composition. In any embodiments, the application may include depositing a first layer of the composition and second layer of the composition to the first layer and, potentially, successive layers thereafter to obtain a 3D article. Such a depositing may include one or more methods, including but not limited to, UV inkjet printing, SLA, continuous liquid interface production (CLIP), and DLP. It is also to be understood that the description of additive manufacturing techniques is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[00169] In some embodiments, the layer of the precursor polymer has a thickness of at least 0.5 μm. In some embodiments, the layer of the precursor polymer has a thickness of at least 1 μm. In some embodiments, the layer of the precursor polymer has a thickness of at least 2 μm. In some embodiments, the layer of the precursor polymer has a thickness of at least 5 μm. In some embodiments, the layer of the precursor polymer has a thickness of at least 10 μm. In some embodiments, the layer of the precursor polymer has a thickness of up to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of up to 40 mm. In some embodiments, the layer of the precursor polymer has a thickness of up to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of up to 1 cm. In some embodiments, the layer of the precursor polymer has a thickness of up to 2 cm. In some embodiments, the layer of the precursor polymer has a thickness of up to 5 cm. In some embodiments, the layer of the precursor polymer has a thickness of up to 10 cm.

[00170] In some embodiments, the layer of the precursor polymer has a thickness of 0.5 μm to 10 cm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 μm to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 40 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 20 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 0.5 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 5 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 1 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 500 µm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 250 µm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 200 µm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 100 µm. In some embodiments, the layer of the precursor polymer has a thickness of 100 µm to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of 200 µm to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of 500 µm to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of 1 mm to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of 100 µm to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of 200 µm to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of 500 µm to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of 1 mm to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of 0.5 µm to 10 µm. In some embodiments, the layer of the precursor polymer has a thickness of 1 µm to 50 µm. In some embodiments, the layer of the precursor polymer has a thickness of 5 µm to 100 µm. In some embodiments, the layer of the precursor polymer has a thickness of 10 µm to 250 µm. In some embodiments, the layer of the precursor polymer has a thickness of 250 µm to 500 µm. In some embodiments, the layer of the precursor polymer has a thickness of 500 µm to 1 mm. In some embodiments, the layer of the precursor polymer has a thickness of 1 mm to 10 mm. In some embodiments, the layer of the precursor polymer has a thickness of 10 mm to 20 mm. In some embodiments, the layer of the precursor polymer has a thickness of 20 mm to 30 mm. In some embodiments, the layer of the precursor polymer has a thickness of 30 mm to 40 mm. In some embodiments, the layer of the precursor polymer has a thickness of 40 mm to 50 mm. In some embodiments, the layer of the precursor polymer has a thickness of 50 mm to 10 cm.

[00171] In some embodiments, the precursor polymer is a solid. In some embodiments, the precursor polymer is a resin. In some embodiments, the precursor polymer is in the form of a layer. In some embodiments the precursor polymer is in the form of a solid layer. In some embodiments, the layer of the precursor polymer is a solid. In some embodiments, the precursor polymer is a solid having a stable shape. In some embodiments, the precursor polymer is a solid having a firm and stable shape. In some embodiments, the layer of the precursor polymer is a solid having a stable shape. In some embodiments, the layer of the precursor polymer is a solid having a firm and stable shape.

[00172] In some embodiments, the layer of the precursor polymer has a percent conversion of at least 50%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 60%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 70%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 75%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 80%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 85%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 90%. In some embodiments, the layer of the precursor polymer has a percent conversion of at least 95%.

[00173] Other applications for the compositions include, but are not limited to, other coating and ink applications for automotive, aerospace, and electronics.

[00174] Some methods described herein include contacting the layers of the composition with ultraviolet light irradiation to induce curing of the composition. In any embodiments, the contacting may include short wavelength and/or long wavelength ultraviolet light irradiation. Suitable short wavelength ultraviolet light irradiation includes UV-C or UV-B irradiation. In one embodiment, the short wavelength ultraviolet light irradiation is UV-C light. Suitable longwave ultraviolet light irradiation includes UV-A irradiation. Additionally, Electron Beam (EB) irradiation may be utilized to induce curing of the composition.

[00175] The methods described herein may include repeating the deposition of layers of the composition and exposure to UV irradiation to obtain the 3D article. In any embodiments, the repeating may occur sequentially wherein depositing the layers of composition is repeated to obtain the 3D article prior to exposure to UV irradiation. In any embodiments, the repeating may occur subsequently wherein the depositing the layers of composition and exposure to UV irradiation are repeated after both steps. In some embodiments, the depositing is performed via UV inkjet printing, stereolithography, continuous liquid interface production, or digital light processing.

[00176] In another related embodiment, a 3D article is provided that includes UV cured successive layers of any of the compositions as described herein. In any embodiments, the composition may have been cast, inkjet, SLA, or DLP deposited.

[00177] In some embodiments, the layer is formed via vat polymerization, material jetting, binder jetting, powder bed fusion, extrusion, directed energy deposition, sheet lamination, extrusion, and/or layer casting. In some embodiments, the layer is formed via UV inkjet printing, stereolithography, continuous liquid interface production, or digital light processing. In some embodiments, the layer is formed via 3D printing.

[00178] In some embodiments, a method provided herein further comprises a step of forming one or more additional layers of the precursor polymer. In some embodiments, the one or more additional layers of the precursor polymer are formed prior to the imidizing step. In some embodiments, the one or more additional layers of the precursor polymer are formed subsequent to the imidizing step. In some embodiments, the one or more additional layers of the precursor polymer undergo imidization. In some embodiments, the one or more additional layers are formed by repeating step (a) provided herein. In some embodiments, the one or more additional layers are formed by repeating steps (a) and (b) provided herein.

[00179] In some embodiments, an imidizing step (*e.g.*, imidization) described herein occurs without foaming. In some embodiments, a method provided herein further comprises a step of foaming the precursor polymer. In some embodiments, the imidizing step (*e.g.*, imidization) is performed prior to, concurrent with, or subsequent to the foaming step. In some embodiments, the imidizing step (*e.g.*, imidization) is performed prior to the foaming step. In some embodiments, the imidizing step (*e.g.*, imidization) is performed concurrently with the foaming step. In some embodiments, the imidizing step (*e.g.*, imidization) is performed subsequent to the foaming step.

[00180] Methods for inducing imidization and foaming include but are not limited to, supplying heat using hot-air convection furnaces, microwave radiation, magnetic induction, infrared radiation, near-infrared radiation, optionally combined with near-infrared dyes such as but not limited to, cyanines, porphyrine dyes, squaraine dyes, phtalocyanines, squarylium salts, diimonium salts, and dithiolene complexes.

[00181] In some embodiments, the imidizing step (*e.g.*, imidization) comprises irradiating the precursor polymer with actinic radiation. In some embodiments, the imidizing step (*e.g.*, imidization) comprises irradiating the precursor polymer with electromagnetic radiation. In some embodiments, the imidizing step (*e.g.*, imidization) comprises irradiating the precursor polymer with electromagnetic radiation as provided herein (e.g., having a wavelength described elsewhere herein, such as wavelength of actinic radiation suitable for polymerization of the monomer formulations described elsewhere herein). In some embodiments, the imidizing step (*e.g.*, imidization) comprises irradiating the precursor polymer with near-infrared radiation. In some embodiments, the imidizing step (*e.g.*, imidization) comprises irradiating the precursor polymer with infrared radiation.

[00182] In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer. In some embodiments, the heating causes the precursor polymer to undergo foaming. In some embodiments, the foaming step comprises heating the precursor polymer. In some embodiments, the foaming step comprises heating the precursor polymer below the T_g of the precursor polymer. In some embodiments, the heat is supplied using conduction, convection, or radiation. In some embodiments, the heat is supplied using a hot-air convection furnace, microwave radiation, magnetic induction, infrared radiation, and/or near-infrared radiation. In some embodiments, the heat is supplied using a furnace, heating element, or water bath. In some embodiments, the heat is supplied using a hot-air convection furnace.

[00183] In some embodiments, the imidizing step (*e.g.*, imidization) is performed prior to the foaming step using a blowing agent that volatilizes or decomposes above the imidization temperature. In some embodiments, the imidizing step (*e.g.*, imidization) is performed concurrently with the foaming step using a blowing agent that volatilizes or decomposes close to the imdization temperature. In some embodiments, the imidizing step (*e.g.*, imidization) is performed concurrently with the foaming step when a blowing agent is generated during the imidizing step (*e.g.*, imidization). In some embodiments, the heating during the imidizing step causes the precursor polymer to undergo foaming. In some embodiments, the imidizing step (*e.g.*, imidization) is performed subsequent to the foaming step using a blowing agent that volatilizes or decomposes below the imidization temperature.

[00184] In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to at least 100 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to at least 120 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to at least 150 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to 100 °C to 250 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to 130 °C to 220 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to 140 °C to 210 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to 150 °C to 200 °C. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer to 160 °C to 190 °C.

[00185] In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 1 second to 4 hours. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 1 minute to 4 hours. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 5 minutes to 4 hours. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 30 seconds to 2 minutes. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 1 minute to 5 minutes. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 5 minutes to 20 minutes. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 20 minutes to 1 hour. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 1 hour to 4 hours. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 20 minutes to 3 hours. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 30 minutes to 2 hours. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 40 minutes to 80 minutes. In some embodiments, the imidizing step (*e.g.*, imidization) comprises heating the precursor polymer for 80 minutes to 120 minutes.

[00186] In some embodiments, at least a portion of the precursor polymer undergoes imidization. In some embodiments, at least 20% of the precursor polymer undergoes imidization. In some embodiments, at least 40% of the precursor polymer undergoes imidization. In some embodiments, at least 60% of the precursor polymer undergoes imidization. In some embodiments, at least 80% of the precursor polymer undergoes imidization. In some embodiments, at least 90% of the precursor polymer undergoes imidization. In some embodiments, at least 95% of the precursor polymer undergoes imidization. In some embodiments, 20%-100% of the precursor polymer undergoes imdization. In some embodiments, 40%-100% of the precursor polymer undergoes imdization. In some embodiments, 60%-100% of the precursor polymer undergoes imdization. In some embodiments, 80%-100% of the precursor polymer undergoes imdization. In some embodiments, the portion of the precursor polymer is a section (*e.g.*, a section of a layer).

[00187] In some embodiments, at least a section of the layer of the precursor polymer undergoes imidization. In some embodiments, the layer of the precursor polymer undergoes imidization in its entirety. In some embodiments, at least a section of one or more layers of the precursor polymer undergo imdidization. In some embodiments, one or more layers of the precursor polymer undergo imdidization in their entirety. In some embodiments, at least a section of one or more layers of the precursor polymer undergo concurrent imdidization. In some embodiments, one or more layers of the precursor polymer undergo concurrent imdidization. In some embodiments, at least a section of one or more layers of the precursor polymer undergo sequential imdidization. In some embodiments, one or more layers of the precursor polymer undergo sequential imdidization. In some embodiments, a columetric section spanning one or more layers of the precursor undergoes imidization. In some embodiments, at least 20% of one or more layers of the precursor polymer undergoes imidization. In some embodiments, at least 40% of one or more layers of the precursor polymer undergoes imidization. In some embodiments, at least 60% of one or more layers of the precursor polymer undergoes imidization. In some embodiments, at least 80% of one or more layers of the precursor polymer undergoes imidization. In some embodiments, at least 90% of one or more layers of the precursor polymer undergoes imidization. In some embodiments, at least 95% of one or more layers of the precursor polymer undergoes imidization. In some embodiments, 20%-100% of one or more layers of the precursor polymer undergoes imdization. In some embodiments, 40%-100% of one or more layers of the precursor polymer undergoes imdization. In some embodiments, 60%-100% of one or more layers of the precursor polymer undergoes imdization. In some embodiments, 80%-100% of one or more layers of the precursor polymer undergoes imdization.

[00188] In some embodiments, the foaming step comprises heating the precursor polymer above the imidization temperature. In some embodiments, the foaming step comprises heating the precursor polymer above 150 °C. In some embodiments, the foaming step comprises heating the precursor polymer above 170 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 150 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 160 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 170 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 180 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 190 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 200 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 150 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 160 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 170 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 180 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 190 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 200 °C to 250 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 150 °C to 200 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 160 °C to 200 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 170 °C to 200 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 180 °C to 200 °C. In some embodiments, the foaming step comprises heating the precursor polymer from 190 °C to 200 °C.

[00189] In some embodiments, the foaming step comprises heating the precursor polymer below the imidization temperature. In some embodiments, the foaming step comprises heating the precursor polymer up to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer up to 150 °C. In some embodiments, the foaming step comprises heating the precursor polymer up to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer up to 130 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 30 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 40 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 50 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 60 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 70 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 80 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 90 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 100 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 110 °C to 160 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 30 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 40 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 50 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 60 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 70 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 80 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 90 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 100 °C to 140 °C. In some embodiments, the foaming step comprises heating the precursor polymer to 110 °C to 140 °C.

[00190] In some embodiments, the foaming step comprises heating the precursor polymer for 5 minutes to 4 hours. In some embodiments, the foaming step comprises heating the precursor polymer for 20 minutes to 3 hours. In some embodiments, the foaming step comprises heating the precursor polymer for 30 minutes to 2 hours. In some embodiments, the foaming step comprises heating the precursor polymer for 40 minutes to 80 minutes. In some embodiments, the foaming step comprises heating the precursor polymer for 80 minutes to 120 minutes. In some embodiments, the foaming step comprises heating the precursor polymer for the duration of the imidizing step (*e.g.*, imidization).

[00191] In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes. Non-limiting examples of suitable near-infrared dyes include cyanine dyes, phtalocyanine dyes, porphyrine dyes, squaraine dyes, squarylium dyes, diimonium dyes, and dithiolene complexes. In some embodiments, the near-infrared dye is a cyanine dye, a phtalocyanine dye, a squarylium dye, a diimonium dye, or a dithiolene complex. In some embodiments, the near-infrared dye is a cyanine dye. In some embodiments, the cyanine dye is IR-813. In some embodiments, the cyanine dye is IR-783. In some embodiments, the near-infrared dye is a near-infrared borate dye or a near-infrared heat generating dye. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises a cyanine dye. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises IR-813, IR-140, IR-780, IR-783, IR-1601, Indocyanine Green, IR-140, IR-780, S2425, S0507, S2544, S0991, S2025, camphorquinone, ethyldimethylaminobenzoate, SQ-1, SQ-2, SQ-3, BODIPY, or a salt thereof. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises IR-813, IR-813 borate, IR-783, IR-140 borate, IR-780 borate, IR-1601, Indocyanine Green, IR-140 perchlorate, IR-780 iodide, S2425, S0507, S2544, S0991, S2025, camphorquinone, ethyldimethylaminobenzoate, SQ-1, SQ-2, SQ-3, or BODIPY.In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises IR-813 or IR-783. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises a dye provided in U.S. patent number 11,384,167, which is incorporated herein by reference.

[00192] In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 1 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 0.5 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 0.4 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 0.3 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 0.2 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 0.1 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.01 wt% to 0.05 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.05 wt% to 0.1 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.1 wt% to 0.5 wt%. In some embodiments, the reaction mixture, a layer of the precursor polymer, and/or a material comprising a precursor polymer comprises one or more near-infrared dyes in an amount of 0.5 wt% to 1 wt%.

[00193] In some embodiments, each side or face of a precursor polymer layer comprising one or more near-infrared dyes described herein is irradiated. In some embodiments, each side or face of a precursor polymer layer comprising one or more near-infrared dyes described herein is irradiated for a similar duration of time.

[00194] In some embodiments, a precursor polymer comprises an optionally substituted polyacrylic ester, an optionally substituted polyacrylamide, an optionally substituted polyacrylic acid, an optionally substituted polyacrylonitrile, and/or any copolymer thereof. In some embodiments, a precursor polymer comprises an optionally substituted polyacrylic ester, an optionally substituted polyacrylamide, an optionally substituted polyacrylic acid, and/or any copolymer thereof. In some embodiments, a precursor polymer comprises an optionally substituted poly(meth)acrylic ester, an optionally substituted poly(meth)acrylamide, an optionally substituted poly(meth)acrylic acid, and/or any copolymer thereof. In some embodiments, a precursor polymer comprises an optionally substituted polyacrylic ester, an optionally substituted polyacrylamide, an optionally substituted polyacrylic acid, an optionally substituted polyacrylonitrile, and/or any copolymer thereof prepared according to a method provided herein.

[00195] Also provided herein are poly(meth)acrylimides prepared according to any method provided herein.

[00196] The obtained PMI materials may be particularly suitable for high temperature applications in their dense and/or foamed states.

[00197] PMI foams can be obtained in densities ranging from 30 kg/m^3 to 600 kg/m^3 and/or may possess homogeneous microstructures. In some embodiments, the PMI foam has a density of 30 kg/m^3 to 600 kg/m^3. In some embodiments, the PMI foam has a density of 30 kg/m^3 to 300 kg/m^3. In some embodiments, the PMI foam has a density of 300 kg/m^3 to 600 kg/m^3. In some embodiments, the PMI foam has a density of 30 kg/m^3 to 100 kg/m^3. In some embodiments, the PMI foam has a density of 100 kg/m^3 to 200 kg/m^3. In some embodiments, the PMI foam has a density of 200 kg/m^3 to 300 kg/m^3. In some embodiments, the PMI foam has a density of 300 kg/m^3 to 400 kg/m^3. In some embodiments, the PMI foam has a density of 400 kg/m^3 to 500 kg/m^3. In some embodiments, the PMI foam has a density of 500 kg/m^3 to 600 kg/m^3.

[00198] In some embodiments, a PMI resin is obtained with a higher density than a PMI foam. In some embodiments, a PMI resin has a density of at least 600 kg/m^3. In some embodiments, the PMI resin has a density of 600 kg/m^3 to 2500 kg/m^3. In some embodiments, the PMI resin has a density of 600 kg/m^3 to 2000 kg/m^3. In some embodiments, the PMI resin has a density of 600 kg/m^3 to 1500 kg/m^3. In some embodiments, the PMI resin has a density of 600 kg/m^3 to 1000 kg/m^3. In some embodiments, the PMI resin has a density of 1000 kg/m^3 to 1500 kg/m^3. In some embodiments, the PMI resin has a density of 1500 kg/m^3 to 2000 kg/m^3. In some embodiments, the PMI resin has a density of 600 kg/m^3 to 900 kg/m^3. In some embodiments, the PMI resin has a density of 900 kg/m^3 to 1200 kg/m^3. In some embodiments, the PMI resin has a density of 1200 kg/m^3 to 1500 kg/m^3. In some embodiments, the PMI resin has a density of 1500 kg/m^3 to 2000 kg/m^3. In some embodiments, the PMI resin has a density of 2000 kg/m^3 to 2500 kg/m^3.

[00199] In some embodiments, the PMI foam has a homogenous microstructure. In some embodiments, a homogenous microstructure is characterized by optical microscopy or electron microscopy. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 1 μm to 500 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 1 μm to 250 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 1 μm to 100 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 1 μm to 50 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 10 μm to 500 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 25 μm to 500 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 50 μm to 500 μm. In some embodiments, a PMI foam having a homogenous microstructure has a pore size of 100 μm to 500 μm. In some embodiments, a homogenous microstructure is characterized by nuclear magnetic resonance spectroscopy. In some embodiments, a homogenous microstructure is characterized by nuclear magnetic resonance spectroscopy by comparing relaxation times of solvent at a surface of a pore to those of solvent in the pore. In some embodiments, a homogenous microstructure is characterized by ultrasound. In some embodiments, a homogenous microstructure is characterized by tomography.

[00200] In particular, for PMI materials produced by some additive manufacturing methods according to this disclosure, geometries are not constrained to rectangular blocks, and/or production times are cut to hours.

[00201] Additionally, the thermomechanical properties of the PMI foams may be particularly improved above 160 °C. In some embodiments, the thermomechanical properties of the PMI foams are improved compared to industrial standards. In some embodiments, the PMI foam has a T_g of at least 160 °C. In some embodiments, the PMI foam has a T_g of at least 170 °C. In some embodiments, the PMI foam has a T_g of at least 180 °C. In some embodiments, the PMI foam has a T_g of at least 190 °C. In some embodiments, the PMI foam has a T_g of 160 °C to 250 °C. In some embodiments, the PMI foam has a T_g of 160 °C to 230 °C. In some embodiments, the PMI foam has a T_g of 160 °C to 220 °C. In some embodiments, the PMI foam has a T_g of 160 °C to 210 °C. In some embodiments, the PMI foam has a T_g of 160 °C to 200 °C. In some embodiments, the PMI foam has a T_g of 160 °C to 170 °C. In some embodiments, the PMI has a T_g of 170 °C to 190 °C. In some embodiments, the PMI foam has a T_g of 190 °C to 210 °C. In some embodiments, the PMI foam has a T_g of 210 °C to 230

°C. In some embodiments, the PMI foam has a T_g of 230 °C to 240 °C. In some embodiments, the PMI foam has a T_g of 240 °C to 250 °C.

[00202] In some embodiments, a PMI resin has increased thermomechanical properties relative to a PMI foam. In some embodiments, the PMI resin has a T_g of at least 160 °C. In some embodiments, the PMI resin has a T_g of at least 170 °C. In some embodiments, the PMI resin has a T_g of at least 180 °C. In some embodiments, the PMI resin has a T_g of at least 190 °C. In some embodiments, the PMI resin has a T_g of at least 200 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 280 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 270 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 260 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 250 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 240 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 200 °C. In some embodiments, the PMI resin has a T_g of 160 °C to 170 °C. In some embodiments, the PMI resin has a T_g of 170 °C to 190 °C. In some embodiments, the PMI resin has a T_g of 190 °C to 200 °C. In some embodiments, the PMI resin has a T_g of 200 °C to 220 °C. In some embodiments, the PMI resin has a T_g of 220 °C to 240 °C. In some embodiments, the PMI resin has a T_g of 240 °C to 260 °C. In some embodiments, the PMI resin has a T_g of 250 °C to 270 °C. In some embodiments, the PMI resin has a T_g of 260 °C to 280 °C.

[00203] In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 5 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 10 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 15 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 20 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 30 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 40 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 50 MPa. In some embodiments, the compressive modulus of a PMI foam produced according to a method provided herein is at least 75 MPa.

[00204] In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 50 MPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 60 MPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 75 MPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 100 MPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 200 MPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 500 MPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 1 GPa. In some embodiments, the flexural modulus of a PMI foam produced according to a method provided herein is at least 5 GPa.

EXAMPLES

[00205] In order that the present disclosure may be more fully understood, the following examples are set forth. The synthetic and biological examples described in this application are offered to illustrate the compounds, pharmaceutical compositions, and methods provided herein and are not to be construed in any way as limiting in their scope.

Comparative Example 1

[00206] A mixture of 13.26 g methacrylic acid, 13.38 g methacrylamide, 0.24 g triallyl isocyanurate, 3.60 g water was stirred until homogeneous. 0.18 g azobisisobutyronitrile was added as thermal initiator and the monomeric mixture was poured into an aluminum mold, sealed, and polymerized at 40 °C for 48 h. The temperature was then increased to 75 °C for 12 h, followed by tempering at 110 °C for 12 h. The obtained rectangular copolymer block was subsequently imidized and foamed at 190 °C in a hot-air furnace for 2 h. The density of the obtained foam was 50 kg/m^3. Compressive modulus measured by DMA at 25 °C was 17 MPa at 25 °C and 18 MPa at 180 °C. Flexural modulus measured by DMA was 28 MPa at 25 °C and 23 at 180 °C.

Example 1

[00207] To a mixture of 5.50 g methacrylic acid, 5.55 g methacrylamide, 1.5 g water, and 0.11 g ethylene glycol dimethacrylate, 1.11 g of a homogenizer that is a copolymer of a (meth)acrylamide and a (meth)acrylic acid ester was added. The mixture was stirred until homogeneous, then 1.11 g urea and 0.33 g diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide were added. The mixture was extruded in a silicone mold as a single layer and photocured with a LED lamp (405 nm,100 W) for 30 s on each side. The obtained copolymer block was subsequently imidized and foamed at 190 °C in a hot-air furnace for 1 h. The density of the obtained PMI foam was 70 kg/m^3. Compressive modulus measured by DMA at 25 °C was 87 MPa at 25 °C. Flexural modulus measured by DMA was 62 MPa at 25 °C.

Example 2

[00208] A monomer mixture comprising 190.45 g methacrylic acid, 192.13 g methacrylamide, 69.00 g water, 26.73 g CN9009 and 2.97 g Photomer 4356 as crosslinkers, and 38.02 g urea as blowing agent was stirred at room temperature until homogeneous. 11.47 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide were added, and the mixture was loaded in a SLA 3D printer with a light source at 405 nm. The obtained 3D printed article was successfully imidized and foamed at 190 °C in a hot-air furnace for 1 h. The density of the obtained PMI foam was 50 kg/m^3. Compressive modulus measured by DMA at 25 °C was 25 MPa at 25 °C and 25 MPa at 180 °C.

Example 3

[00209] To a mixture of 5.50 g methacrylic acid, 5.55 g methacrylamide, 1.5 g water, and 0.11 g ethylene glycol dimethacrylate. The mixture was stirred until homogeneous, 0.33 g diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide were added. The mixture was extruded in a silicone mold as a single layer and photocured with a LED lamp (405 nm,100 W) for 30 s on each side. The obtained copolymer block was subsequently imidized at 160 °C for 1 h, followed by thermal treatment at 180 °C for 2 h in a hot-air furnace. The density of the obtained PMI polymer was 1324 kg/m^3. Flexural modulus measured by DMA was 6.5 GPa at 25 °C.

PMI Foams

Example 4

[00210] A mixture of 11.90 g methacrylic acid, 11.90 g methacrylamide, 4.40 g water, 1.00 g glycerol, 2.00 g urea and 0.28 g ethylene glycol dimethacrylate (EGDMA) was stirred at 40 °C until homogenous. 0.70 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution was layer-casted in a rectangular silicone mold (100 mm x 10 mm x 10 mm) to form a 1 mm thick liquid layer. The layer was photocured for 40 seconds with a 365 nm LED (40 mW/cm^2) on one side, then flipped and photocured again for 40 seconds on the other side. The obtained transparent yellow rectangular copolymer was imidized and foamed at 180 °C for 1h in a hot-air furnace. The obtained PMI foam had a density of 250 kg/m^3 and a T_g of 172 °C.

Example 5

[00211] A mixture of 11.90 g methacrylic acid, 11.90 g methacrylamide, 4.40 g water, 1.00 g glycerol, 2.50 g N-methylurea and 0.10 g trimethylolpropane trimethacrylate (TMPTMA) was stirred at 40 °C until homogenous. 0.70 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution was layer-casted in a rectangular silicone mold (100 mm x 10 mm x 10 mm) to form a 1 mm thick liquid layer. The layer was photocured for 40 seconds with a 365 nm LED (40 mW/cm^2) on one side, then flipped and photocured again for 40 seconds on the other side. The obtained transparent rectangular copolymer was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 160 kg/m^3 and a T_g of 171 °C.

Example 6

[00212] The same reaction mixture of Example 5 was loaded in a LCD 3D printer with a light source at 405 nm and irradiance of 2 mW/cm^2. A rectangular (60 mm x 10 mm x 5 mm) 3D article was printed by sequentially photocuring 50 μm thick layers with 10 seconds exposure. The copolymer block was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 150 kg/m^3 and a T_g of 170 °C.

Example 7

[00213] A mixture of 11.90 g methacrylic acid, 11.90 g methacrylamide, 4.40 g water, 1.00 g glycerol, 2.00 g urea, 0.20 g tris(2-hydroxyethyl)isocyanurate triacrylate (THEICTA) and 1.80 g urethane dimethacrylate (UDMA) was stirred at 40 °C until homogenous. 0.70 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution was layer-casted in a rectangular silicone mold (100 mm x 10 mm x 10 mm) to form a 2 mm thick liquid layer. The layer was photocured for 40 seconds with a 405 nm LED (32 mW/cm2) on one side, then flipped and photocured again for 40 seconds on the other side. The obtained transparent yellow rectangular copolymer was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 478 kg/m^3 and a T_g of 165 °C.

Example 8

[00214] A mixture of 23.80 g methacrylic acid, 23.80 g methacrylamide, 8.80 g water, 2.00 g glycerol, 4.00 g urea and 0.20 g trimethylolpropane trimethacrylate (TMPTMA) was stirred at 40 °C until homogenous. 1.40 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution was loaded in a LCD

3D printer with a light source at 405 nm and irradiance of 2 mW/cm^2. A rectangular (60 mm x 10 mm x 3 mm) 3D article was printed by sequentially photocuring 50 μm thick layers with 10 seconds exposure. The copolymer block was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 80 kg/m^3 and a T_g of 180 °C.

Example 9

[00215] A mixture of 23.80 g methacrylic acid, 23.80 g methacrylamide, 8.80 g water, 2.00 g glycerol, 4.00 g urea, 0.30 g tris(2-hydroxyethyl)isocyanurate triacrylate (THEICTA) and 1.60 g urethane dimethacrylate (UDMA) was stirred at 40 °C until homogenous. 1.40 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution was loaded in a LCD 3D printer with a light source at 405 nm and irradiance of 2 mW/cm^2. A rectangular (60 mm x 10 mm x 3 mm) 3D article was printed by sequentially photocuring 50 μm thick layers with 10 seconds exposure. The copolymer block was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 120 kg/m^3 and a T_g of 172 °C.

Example 10

[00216] A mixture of 18.00 g methacrylic acid, 12.00 g methacrylamide, 3.00 g butylmethacrylate, 3.00 g water, 3.00 g urea, 0.30 g ethylene glycol dimethacrylate (EGDMA) was stirred at 40 °C until homogenous. 0.92 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution was layer-casted in a rectangular silicone mold (100 mm x 10 mm x 10 mm) to form a 2 mm thick liquid layer. The layer was photocured for 40 seconds with a 405 nm LED (32 mW/cm^2) on one side, then flipped and photocured again for 40 seconds on the other side. The obtained transparent yellow rectangular copolymer was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 220 kg/m^3 and a T_g of 170 °C.

Example 11

[00217] A mixture of 27.00 g methacrylic acid, 18.00 g methacrylamide, 4.50 g butylmethacrylate, 4.50 g water, 4.50 g urea, 0.40 g triethylene glycol dimethacrylate (TEGDMA) was stirred at 40 °C until homogenous. 1.38 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were added, and after cooling to room temperature, the clear solution layer-casted in a rectangular silicone mold (100 mm x 10 mm x 10 mm) to form a 1 mm thick liquid layer. The layer was photocured for 40 seconds with a 365 nm LED

(40 mW/cm^2) on one side, then flipped and photocured again for 40 seconds on the other side. The obtained transparent yellow rectangular copolymer was imidized and foamed at 180 °C for 1 h in a hot-air furnace. The obtained PMI foam had a density of 68 kg/m^3 and a T_g of 172 °C.

PMI Resins

Example 12

[00218] A monomer mixture comprising 42.86 g methacrylic acid, 23.06 g methacrylamide, 17.30 g N-hydroxyethyl acrylamide and 14.51 g of a polyester acrylate crosslinker was stirred at room temperature until homogeneous. 11.47 g Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide were added, and after cooling to room temperature, the clear solution was layer-casted in a rectangular silicone mold (100 mm x 10 mm x 10 mm) to form a 2 mm thick liquid layer. The layer was photocured for 40 seconds with a 405 nm LED (32 mW/cm^2) on one side, then flipped and photocured again for 40 seconds on the other side. The obtained clear yellow rectangular copolymer was imidized and foamed at 190 °C for 2 h in a hot-air furnace. The obtained PMI resin had a density of 1230 kg/m^3 and a T_g of 190 °C.

Near-Infrared Dyes

Example 13

[00219] Temperature response in precursor polymers and poly(meth)acrylimides was measured over time upon exposure to near-infrared (NIR) irradiation with a 810 nm LED array operated at different irradiances (**FIGs. 3-10**). The temperature was measured on the irradiated surface of a polymer sample with an infrared camera. Polymer samples containing different %wt of NIR dyes were tested and compared to a control sample of the same polymer without dyes. NIR dyes tested were IR-813 (**FIGs. 3-7**) and IR-783 (**FIGs. 8-10**). In the case of poly(meth)acrylimide materials, when the polymer surface starts to foam, the surface becomes a thermal insulator, and a drop in temperature is observed in the measured curves. The higher the concentration of the dyes at same irradiance, the faster is the temperature increase. The photothermal effect of the NIR dyes and the measured temperature plateau after a certain amount of time.

EQUIVALENTS AND SCOPE

[00220] In the claims articles such as “a,” “an,” and “the” may mean one or more than one unless indicated to the contrary or otherwise evident from the context. Claims or descriptions that include “or” between one or more members of a group are considered satisfied if one, more than one, or all of the group members are present in, employed in, or otherwise relevant to a given product or process unless indicated to the contrary or otherwise evident from the context. The present disclosure includes embodiments in which exactly one member of the group is present in, employed in, or otherwise relevant to a given product or process. The present disclosure includes embodiments in which more than one, or all of the group members are present in, employed in, or otherwise relevant to a given product or process.

[00221] Furthermore, the present disclosure encompasses all variations, combinations, and permutations in which one or more limitations, elements, clauses, and descriptive terms from one or more of the listed claims is introduced into another claim. For example, any claim that is dependent on another claim can be modified to include one or more limitations found in any other claim that is dependent on the same base claim. Where elements are presented as lists, e.g., in Markush group format, each subgroup of the elements is also disclosed, and any element(s) can be removed from the group. It should it be understood that, in general, where the present disclosure, or aspects or embodiments of the present disclosure, is/are referred to as comprising particular elements and/or features, certain embodiments of the present disclosure or aspects or embodiments of the present disclosure consist, or consist essentially of, such elements and/or features. For purposes of simplicity, those embodiments have not been specifically set forth in haec verba herein. It is also noted that the terms “comprising” and “containing” are intended to be open and permits the inclusion of additional elements or steps. Where ranges are given, endpoints are included. Furthermore, unless otherwise indicated or otherwise evident from the context and understanding of one of ordinary skill in the art, values that are expressed as ranges can assume any specific value or sub-range within the stated ranges in different embodiments of the present disclosure, to the tenth of the unit of the lower limit of the range, unless the context clearly dictates otherwise.

[00222] This application refers to various issued patents, published patent applications, journal articles, and other publications, all of which are incorporated herein by reference. If there is a conflict between any of the incorporated references and the instant specification, the specification shall control. In addition, any particular embodiment of the present disclosure that falls within the prior art may be explicitly excluded from any one or more of the claims. Because such embodiments are deemed to be known to one of ordinary skill in the art, they may be excluded even if the exclusion is not set forth explicitly herein. Any particular embodiment of the present disclosure can be excluded from any claim, for any reason, whether or not related to the existence of prior art.

[00223] Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation many equivalents to the specific embodiments described herein. The scope of the present embodiments described herein is not intended to be limited to the above Description, but rather is as set forth in the appended claims. Those of ordinary skill in the art will appreciate that various changes and modifications to this description may be made without departing from the spirit or scope of the present disclosure, as defined in the following claims.

CLAIMS

What is claimed is:

1. A method of preparing a poly(meth)acrylimide, the method comprising the steps of:
   (a) irradiating a reaction mixture with radiation to form a solid layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

   at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

   the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

   the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

   (b) imidizing at least a section of the solid layer of the precursor polymer to generate the poly(meth)acrylimide.

2. A method of preparing a poly(meth)acrylimide, the method comprising the steps of:
   (a) irradiating a reaction mixture with radiation to form a layer of a precursor polymer, the radiation comprising actinic radiation, wherein:

   at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

   the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

   the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

   at the end of the irradiation, the reaction mixture has a percent conversion of at least 40%;

   (b) imidizing at least a section of the layer of the precursor polymer to generate the poly(meth)acrylimide.

3. A method of preparing a poly(meth)acrylimide, the method comprising the steps of:
   (a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein:

   at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

   at the start of the irradiation, a percent conversion of the reaction mixture is less than 10%;

   the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

   the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

   at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 20%;

   (b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

4. A method of preparing a poly(meth)acrylimide, the method comprising the steps of:
   (a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein:

   at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules;

   the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer;

   the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and

   (b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

5. A method of preparing a poly(meth)acrylimide, the method comprising the steps of:
   (a) irradiating a reaction mixture with radiation comprising actinic radiation to form a precursor polymer, wherein:

at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules, a near-infrared dye, and an initiator,

the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer, and

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 2500 nm; and

(b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

6. A method of preparing a poly(meth)acrylimide, the method comprising:

irradiating a material comprising a precursor polymer and a near-infrared dye with radiation comprising actinic radiation to imidize at least a portion of the precursor polymer to generate the poly(meth)acrylimide,

wherein:

the precursor polymer comprises an optionally substituted polyacrylic ester, an optionally substituted polyacrylamide, an optionally substituted polyacrylic acid, optionally substituted polyacrylonitrile, or any copolymer thereof, and

the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 2500 nm.

7. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises an optionally substituted acrylamide monomer, an optionally substituted acrylic ester monomer, and/or an optionally substituted acrylic acid monomer.

8. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises an optionally substituted acrylate monomer and an optionally substituted acrylamide monomer.

9. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises an optionally substituted acrylamide and an optionally substituted acrylic ester.

10. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises an optionally substituted acrylamide and an optionally substituted acrylic acid.

11. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl acrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isobornyl methacrylate, isobornyl acrylate, glycidyl acrylate, glycidyl methacrylate, dicyclopentanyl acrylate, and/or dicyclopentanyl methacrylate.

12. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises acrylamide, methacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-butylacrylamide, N-[3-(dimethylamino)propyl]acrylamide, 4-acryloylmorpholine, N-[2-(dimethylamino)ethyl]acrylamide, N-[2-(diethylamino)ethyl]acrylamide, diacetone acrylamide, N-(2-hydroxyethyl)acrylamide, N-isopropylacrylamide, N-propylacrylamide, N-(2-amino-2-oxoethyl)acrylamide, N-tert-butylacrylamide, N-(hydroxymethyl)acrylamide, and/or 3-acryloyl-2-oxazolidinone.

13. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises methacrylic acid and methacrylamide.

14. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises an optionally substituted acrylonitrile and an optionally substituted acrylic acid.

15. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises an optionally substituted acrylonitrile and an optionally substituted acrylic ester.

16. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises acrylonitrile or methacrylonitrile and an optionally substituted acrylic acid.

17. The method of any one of the preceding claims, wherein the plurality of monomer molecules comprises acrylonitrile or methacrylonitrile and an optionally substituted acrylic ester.

18. The method of any one of the preceding claims, wherein the reaction mixture further comprises one or more photoinitiators.

19. The method of any one of the preceding claims, wherein the one or more photoinitiators comprise a benzoin ether, a benzil ketal, an α-dialkoxy-acetophenone, an α-hydroxy-alkylphenone, an α-amino alkylphenone, an acyl phosphine oxide, a benzophenone, a thioxanthone, and/or a metallocene.

20. The method of any one of the preceding claims, wherein the one or more photoinitiators comprise acetophenone, anisoin, anthraquinone, anthraquinone-2-sulfonic acid, benzene tricarbonylchromium, benzil, benzoin, benzoin ethyl ether, benzoin methyl ether, benzophenone, 1-hydroxycyclohexyl phenyl ketone, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4-benzoylbiphenyl, 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone, 4,4'-bis(diethylamino)benzophenone, 4,4'-bis(dimethylamino)benzophenone, camphorquinone, 2-chlorothioxanthene-9-one, (cumene)cyclopentadienyl iron(ii) hexafluorophosphate, dibenzosuberenone, 2,2-diethoxyacetophenone, 4,4'-dihydroxybenzophenone, 2,2-dimethoxy-2-phenylacetophenone, 4-(dimethylamino)benzophenone, 4,4'-dimethylbenzil, 2,5-dimethylbenzophenone, 3,4-dimethylbenzophenone, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, 2-hydroxy-2-methylpropiophenone, 4'-ethoxyacetophenone, 2-ethylanthraquinone, ferrocene, 3'-hydroxyacetophenone, 4'-hydroxyacetophenone, 3-hydroxybenzophenone, 4-hydroxybenzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methylpropiophenone, 2-methylbenzophenone, 3-methylbenzophenone, methylbenzoylformate, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, phenanthrenequinone, 4'-

phenoxyacetophenone, thioxanthene-9-one, triarylsulfonium hexafluoroantimonate salts, and/or triarylsulfonium hexafluorophosphate salts.

21. The method of any one of the preceding claims, wherein the one or more photoinitiators comprise diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

22. The method of any one of the preceding claims, wherein the reaction mixture further comprises one or more solvents.

23. The method of any one of the preceding claims, wherein the one or more solvents comprise 1% to 35% of the reaction mixture by weight.

24. The method of any one of the preceding claims, wherein the one or more solvents comprise 5% to 20% of the reaction mixture by weight.

25. The method of any one of the preceding claims, wherein the one or more solvents comprise 8% to 15% of the reaction mixture by weight.

26. The method of any one of the preceding claims, wherein the one or more solvents comprise water.

27. The method of any one of the preceding claims, wherein the reaction mixture further comprises one or more cross-linkers.

28. The method of any one of the preceding claims, wherein the one or more cross-linkers comprise ethylene glycol dimethacrylate, CN9009, or photomer 4356.

29. The method of any one of the preceding claims, wherein the reaction mixture further comprises a homogenizer.

30. The method of any one of the preceding claims, wherein the reaction mixture is homogenous.

31. The method of any one of the preceding claims, wherein the reaction mixture further comprises one or more blowing agents.

32. The method of any one of the preceding claims, wherein the one or more blowing agents comprise urea.

33. The method of any one of the preceding claims, wherein the actinic radiation comprises electron beam radiation.

34. The method of any one of the preceding claims, wherein the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm.

35. The method of any one of the preceding claims, wherein the actinic radiation comprises electromagnetic radiation having a wavelength of greater than 400 nm to less than 410 nm.

36. The method of any one of the preceding claims, wherein the actinic radiation comprises electromagnetic radiation having an irradiance of 1 mW/cm^2 to 50 mW/cm^2.

37. The method of any one of the preceding claims, wherein the irradiation of a reaction mixture is performed at a temperature less than 50 °C.

38. The method of any one of the preceding claims, wherein the irradiation of a reaction mixture is performed at a temperature of 20 °C to 25 °C.

39. The method of any one of the preceding claims, wherein the layer of the precursor polymer further comprises one or more blowing agents.

40. The method of any one of the preceding claims, wherein the one or more blowing agents comprises urea.

41. The method of any one of the preceding claims, wherein the solid layer of the precursor polymer has a thickness of at least 0.5 µm.

42. The method of any one of the preceding claims, wherein the layer of the precursor polymer has a thickness of at least 10 μm.

43. The method of any one of the preceding claims, wherein the layer of the precursor polymer is a solid.

44. The method of any one of the preceding claims, wherein the layer of the precursor polymer has a percent conversion of at least 50%.

45. The method of any one of the preceding claims, wherein the layer of the precursor polymer has a percent conversion of at least 80%.

46. The method of any one of the preceding claims, wherein at the start of the irradiation, the reaction mixture has a percent conversion of less than 5%.

47. The method of any one of the preceding claims, wherein at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 10%.

48. The method of any one of the preceding claims, wherein at least a portion of the precursor polymer undergoes imidization.

49. The method of any one of the preceding claims, wherein at least a section of the layer of the precursor polymer undergoes imidization.

50. The method of any one of the preceding claims, wherein at least 80% of the precursor polymer undergoes imidization.

51. The method of any one of the preceding claims, wherein at least 80% of the layer of the precursor polymer undergoes imidization.

52. The method of any one of the preceding claims, wherein the imidizing step comprises irradiating the precursor polymer with actinic radiation.

53. The method of any one of the preceding claims, wherein the imidizing step comprises irradiating the precursor polymer with electromagnetic radiation.

54. The method of any one of the preceding claims, wherein the imidizing step comprises irradiating the precursor polymer with electromagnetic radiation having a wavelength of 750 nm to 4500 nm.

55. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer.

56. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer to 100 °C to 250 °C.

57. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer to 130 °C to 220 °C.

58. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer to 140 °C to 210 °C.

59. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer to at least 150 °C.

60. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer to 150 °C to 200 °C.

61. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer to 160 °C to 190 °C.

62. The method of any one of the preceding claims, wherein the imidizing step comprises heating the precursor polymer for 30 minutes to 2 hours.

63. The method of any one of the preceding claims, wherein the heating during the imidizing step causes the precursor polymer to undergo foaming.

64. The method of any one of the preceding claims, wherein the method further comprises a step of foaming the precursor polymer.

65. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer.

66. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer below the glass transition temperature (T_g) of the precursor polymer.

67. The method of any one of the preceding claims, wherein the imidizing step is performed prior to the foaming step.

68. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer above 150 °C.

69. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer above 170 °C.

70. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer from 150 °C to 300 °C.

71. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer from 170 °C to 250 °C.

72. The method of any one of the preceding claims, wherein the imidizing step is performed concurrently with the foaming step.

73. The method of any one of the preceding claims, wherein the imidizing step is performed subsequent to the foaming step.

74. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer up to 160 °C.

75. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer up to 140 °C.

76. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer to 50 °C to 160 °C.

77. The method of any one of the preceding claims, wherein the foaming step comprises heating the precursor polymer to 100 °C to 140 °C.

78. The method of any one of the preceding claims, wherein the near-infrared dye is a cyanine dye, a phtalocyanine dye, a squarylium dye, a diimonium dye, or a dithiolene complex.

79. The method of any one of the preceding claims, wherein the near-infrared dye is a cyanine dye.

80. The method of any one of the preceding claims, wherein the cyanine dye is IR-813.

81. The method of any one of the preceding claims, wherein the initiator is a thermal initiator.

82. The method of any one of the preceding claims, wherein the thermal initiator is one or more of tert-amyl peroxybenzoate, 4,4-azobis(4-cyanovaleric acid), 1,1’-azobis(cyclohexanecarbonitrile), 2,2’-azobisisobutyronitrile, benzoyl peroxide, 2,2-bis(tert-butylperoxy)butane, 1,1-bis(tert-butylperoxy)cyclohexane, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, 2,5-bis(tert-butylperoxy)-2,5-dimethyl-3-hexyne, bis(1-(tert-butylperoxy)-1-methylethyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, tert-butyl hydroperoxide, tert-butyl peracetate, tert-butyl peroxide, tert-butyl peroxybenzoate, tert-butylperoxy isopropyl carbonate, cumene hydroperoxide, cyclohexanone peroxide, dicumyl peroxide, lauroyl peroxide, 2,4-pentanedione peroxide, peracetic acid, and/or potassium persulfate.

83. The method of any one of the preceding claims, wherein the initiator is a salt.

84. The method of any one of the preceding claims, wherein the initiator is an onium salt.

85. The method of any one of the preceding claims, wherein the initiator is an iodonium salt or a sulfonium salt.

86. The method of any one of the preceding claims, wherein the initiator is an iodonium salt or a sulfonium salt of formula $(R_A)_2I^+X_A{}^-$ or $(R_A)_3S^+X_A{}^-$; wherein each instance of R_A is independently optionally substituted C_{6-10} aryl or optionally substituted C_{1-10} alkyl; and $X_A{}^-$ is a counter ion.

87. The method of any one of the preceding claims, wherein the initiator is bis(2,4,6-trimethylpyridine)iodonium hexafluorophosphate, bis(4-tert-butylphenyl)iodonium hexafluorophosphate, bis(4-bromophenyl)iodonium trifluoromethanesulfonate, bis(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (3-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate, bis(4-tert-butylphenyl)iodonium tetrafluoroborate, bis(4-tert-butylphenyl)iodonium nonafluoro-1-butanesulfonate, bis(4-tert-butylphenyl)iodonium chloride, diphenyliodonium perchlorate, diphenyliodonium trifluoromethanesulfonate, diphenyliodonium chloride, diphenyliodonium bromide, diphenyliodonium-2-carboxylate monohydrate, 4-Isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate, (2-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (3-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (4-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, (4-Nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate, Phenyl[3-(trifluoromethyl)phenyl]iodonium trifluoromethanesulfonate, [3-(trifluoromethyl)phenyl](2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, [4-(trifluoromethyl)phenyl](2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, bis(4-fluorophenyl)iodonium trifluoromethanesulfonate, diphenyliodonium hexafluorophosphate, [4-fluoro-3-(trifluoromethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, bis(pyridine)iodonium tetrafluoroborate, 4-biphenylyl(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate, (3,5-dichlorophenyl)(2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, (5-fluoro-2-nitrophenyl)(2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, [(4-trifluoromethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, phenyl(2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, [4-

(bromomethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate, or diphenyliodonium nitrate.

88. The method of any one of the preceding claims, wherein the reaction mixture further comprises a reducing agent.

89. The method of any one of the preceding claims, wherein the reducing agent is a phosphine-based reducing agent or an amine-based reducing agent.

90. The method of any one of the preceding claims, wherein the reducing agent is 4-(diphenylphosphino)benzoic acid, 2-diphenylphosphinobenzoic acid, bis(2-diphenylphosphinophenyl)-ether, triomethoxyphenylphosphine, DPBP bidentate phosphine, 4-dimethylaminophenyldiphenylphosphine, (R,R) dach phenyl trost, triphenylphosphine, ethyl 4-dimethylaminobenzoate, 4-(dimethylamino)phenylacetic acid, triphenylamine, N,N-dibutylaniline, N-Ethyl-N-isopropylaniline, or 3-(dimethylamino)benzyl alcohol.

91. The method of any one of the preceding claims, wherein the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 750 nm and less than or equal to 1000 nm.

92. The method of any one of the preceding claims, wherein the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 1000 nm and less than or equal to 1500 nm.

93. The method of any one of the preceding claims, wherein the precursor polymer comprises an optionally substituted polyacrylic ester, an optionally substituted polyacrylamide, an optionally substituted polyacrylic acid, and/or any copolymer thereof.

94. The method of any one of the preceding claims, further comprising a step of preparing the precursor polymer by heating or irradiating a reaction mixture comprising a plurality of monomer molecules, wherein the plurality of monomer molecules comprises an optionally substituted acrylate monomer, an optionally substituted acrylamide monomer, and/or an optionally substituted acrylonitrile monomer.

95. The method of any one of the preceding claims, wherein the layer is formed via vat polymerization, material jetting, binder jetting, powder bed fusion, extrusion, directed energy deposition, sheet lamination, extrusion, and/or layer casting.

96. The method of any one of the preceding claims, wherein the layer is formed via UV inkjet printing, stereolithography, continuous liquid interface production, or digital light processing.

97. The method of any one of the preceding claims, wherein the layer is formed via 3D printing.

98. The method of any one of the preceding claims, further comprising a step of forming one or more additional layers of the precursor polymer.

99. The method of any one of the preceding claims, wherein the one or more additional layers of the precursor polymer are formed prior to the imidizing step.

100. The method of any one of the preceding claims, wherein the one or more additional layers of the precursor polymer are formed subsequent to the imidizing step.

101. The method of any one of the preceding claims, wherein the one or more additional layers of the precursor polymer undergo imidization.

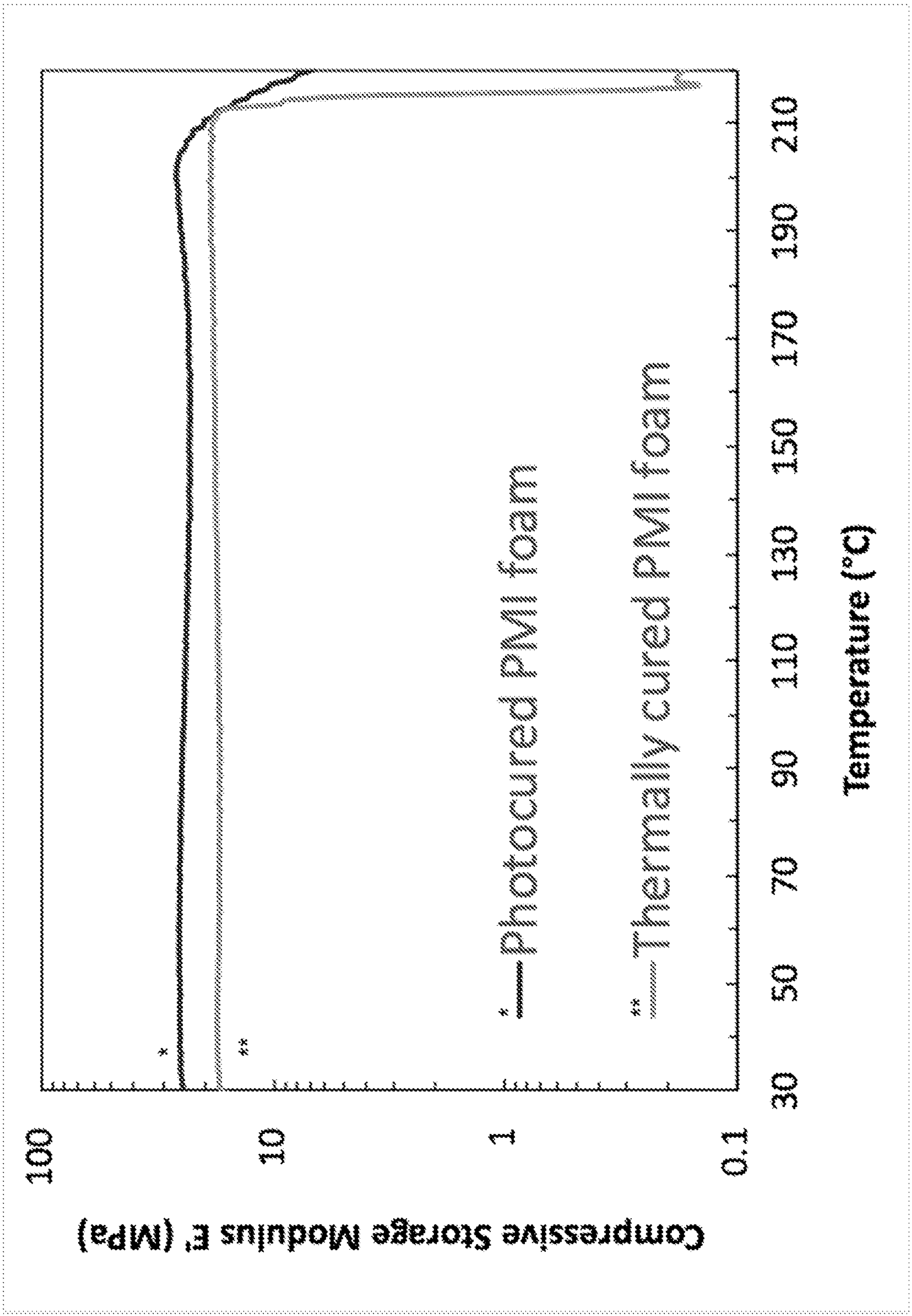
102. The method of any one of the preceding claims, wherein the one or more additional layers are formed by repeating step (a).

103. The method of any one of the preceding claims, wherein the one or more additional layers are formed by repeating steps (a) and (b).

104. The method of any one of the preceding claims, wherein the layer is formed via vat polymerization, material jetting, binder jetting, powder bed fusion, extrusion, directed energy deposition, sheet lamination, extrusion, and/or layer casting.

105. The method of any one of the preceding claims, wherein the depositing is performed via UV inkjet printing, stereolithography, continuous liquid interface production, or digital light processing.

106. A poly(meth)acrylimide prepared according to the method of any one of the preceding claims.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100
10
1
0.1
30
50
70
90
110
130
150
170
190
210
Temperature (°C)
*
**
*—Photocured PMI foam
**—Thermally cured PMI foam

FIG. 1

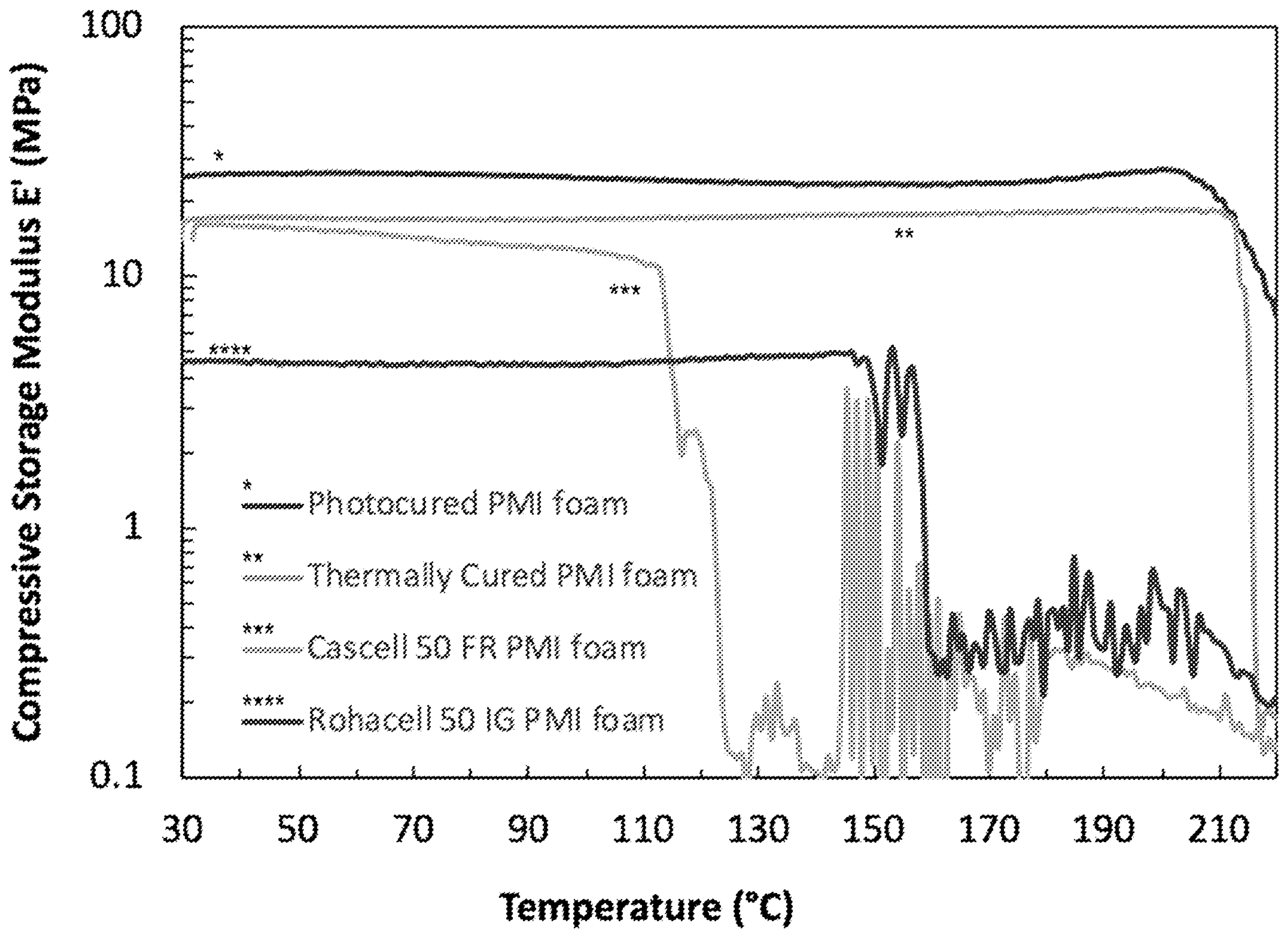
Compressive Storage Modulus E' (MPa)
100
10
1
0.1
30
50
70
90
110
130
150
170
190
210
Temperature (°C)
*
**
***
****
* Photocured PMI foam
** Thermally Cured PMI foam
*** Cascell 50 FR PMI foam
**** Rohacell 50 IG PMI foam

FIG. 2

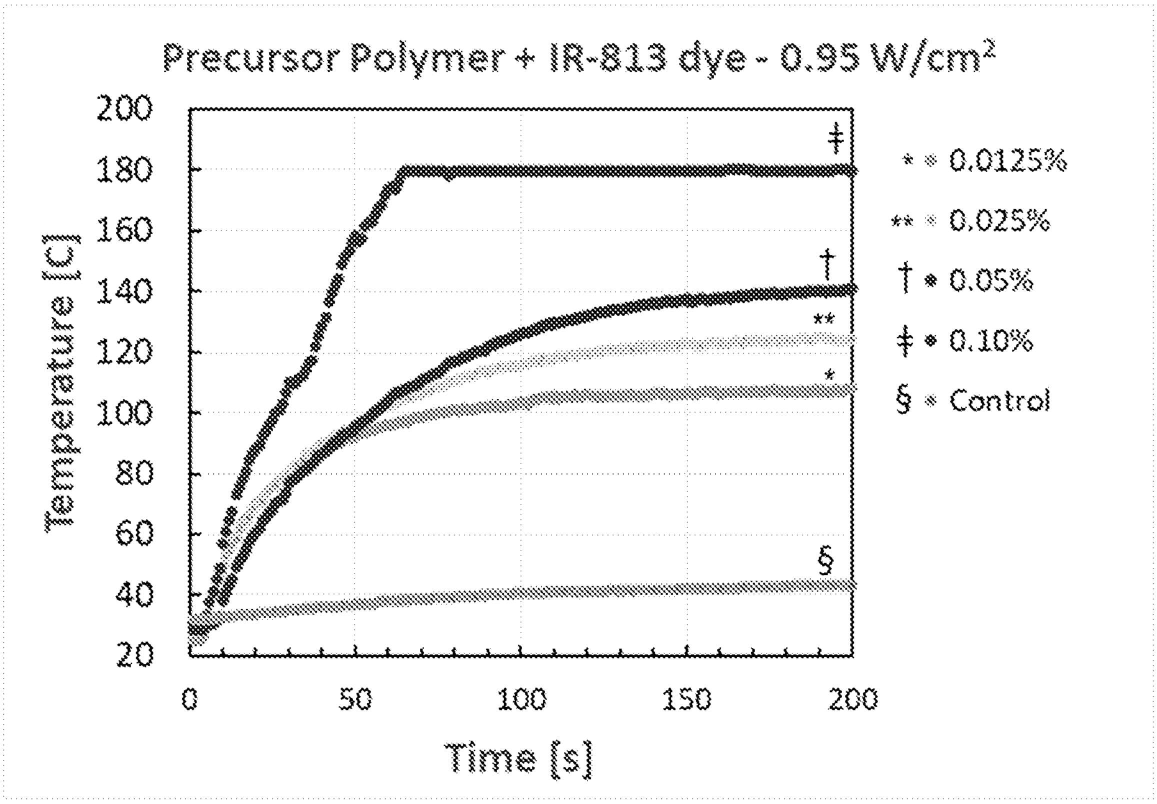
Precursor Polymer + IR-813 dye - 0.95 W/cm²
Temperature [C]
Time [s]
200
180
160
140
120
100
80
60
40
20
0
50
100
150
200
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 3

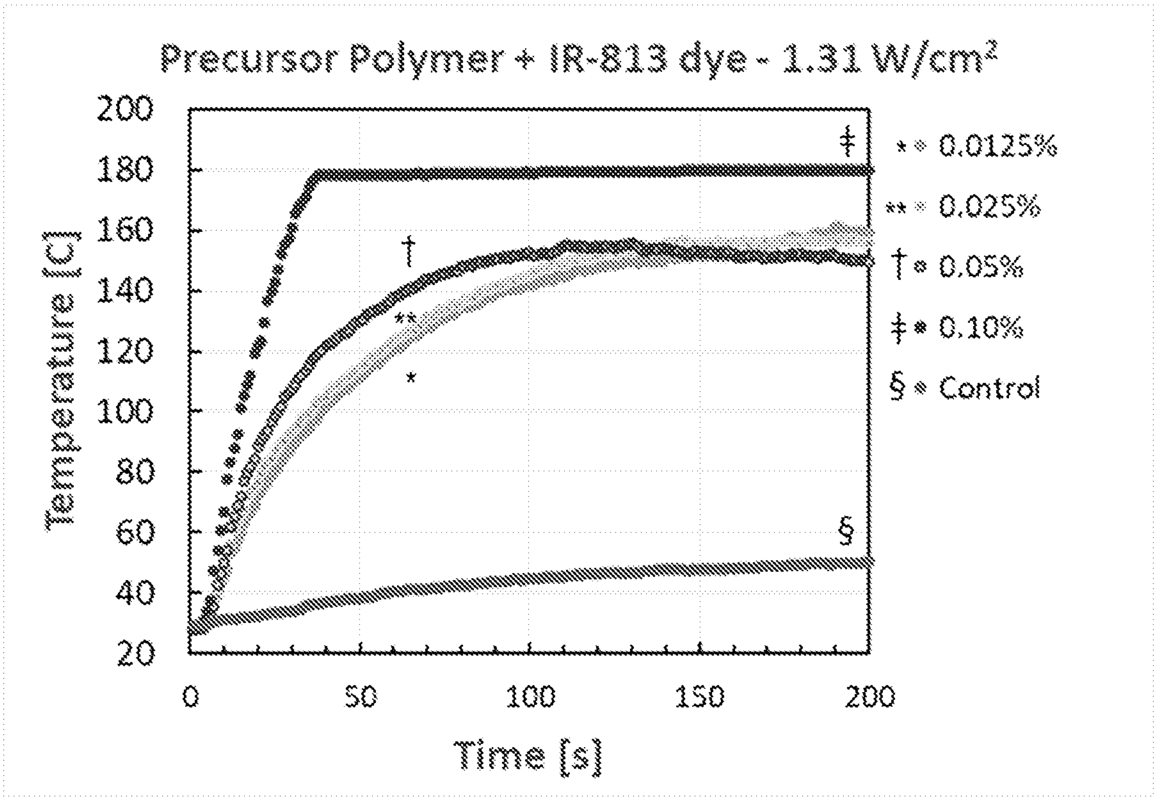
Precursor Polymer + IR-813 dye - 1.31 W/cm²
Temperature [C]
Time [s]
200
180
160
140
120
100
80
60
40
20
0
50
100
150
200
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 4

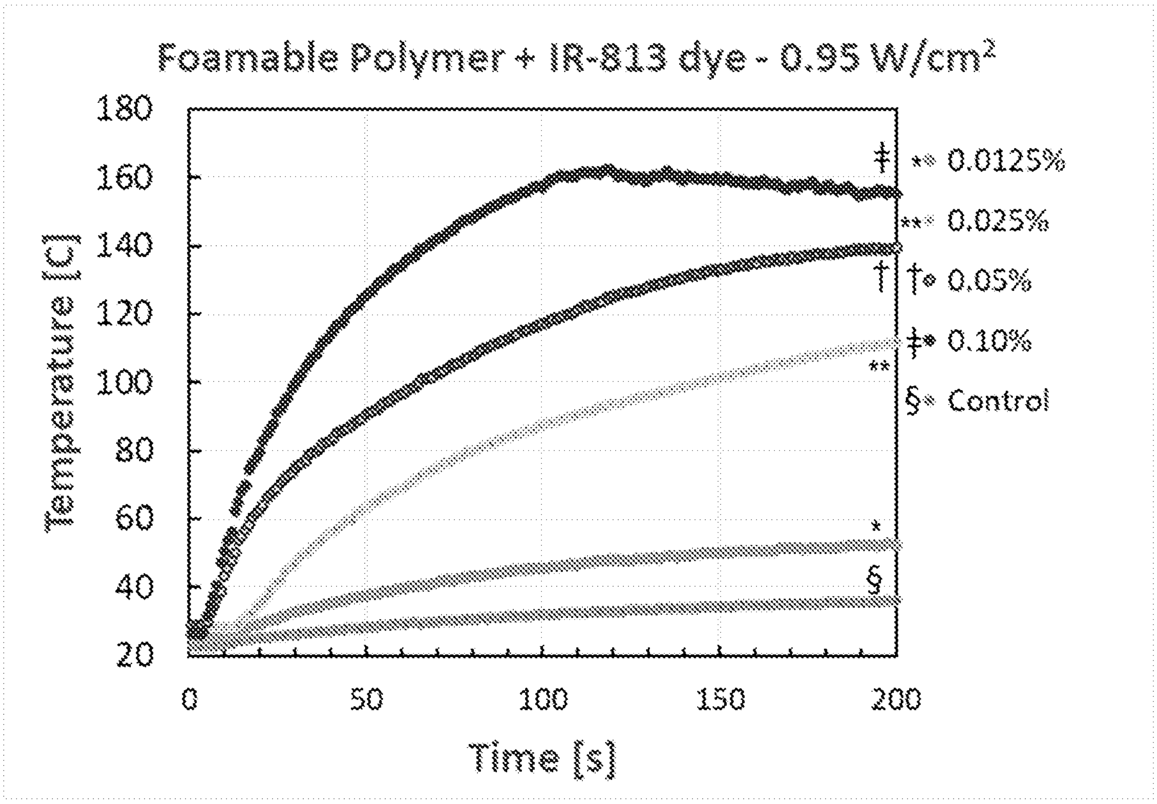
Foamable Polymer + IR-813 dye - 0.95 W/cm²
Temperature [C]
Time [s]
180
160
140
120
100
80
60
40
20
0
50
100
150
200
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 5

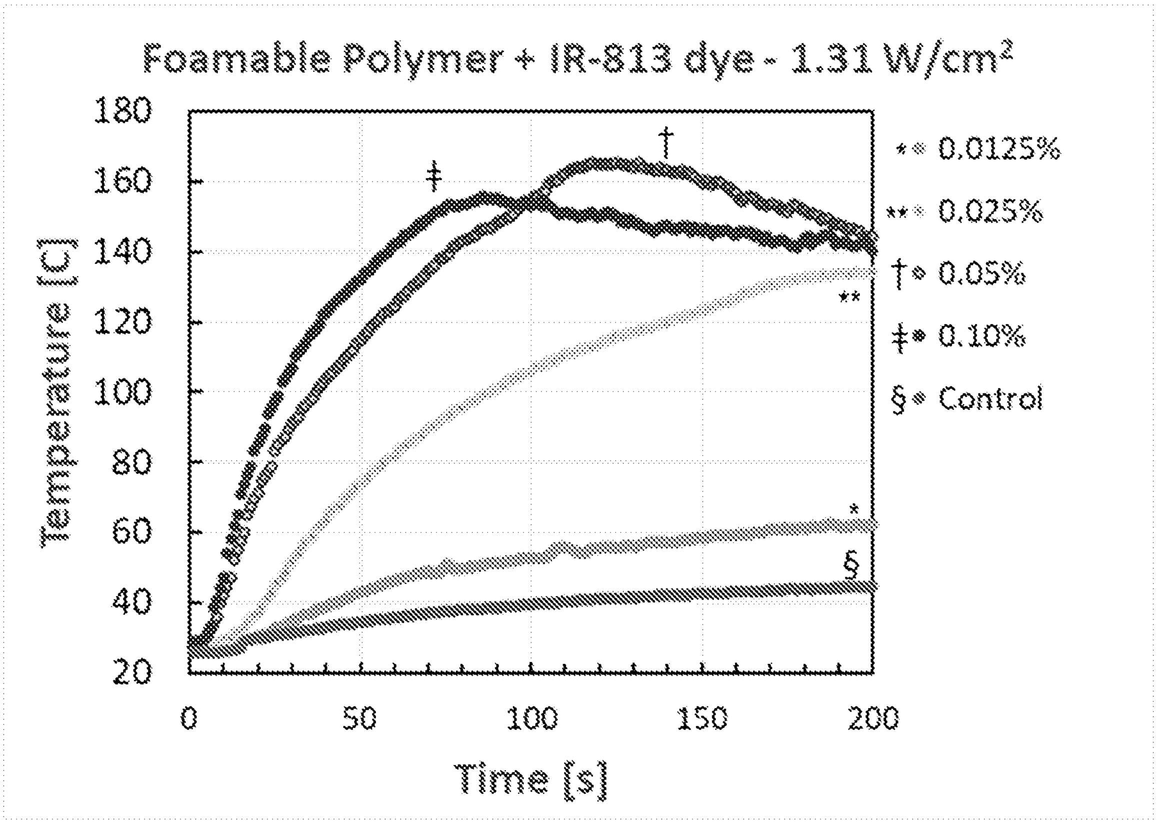
Foamable Polymer + IR-813 dye - 1.31 W/cm²
Temperature [C]
Time [s]
180
160
140
120
100
80
60
40
20
0
50
100
150
200
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 6

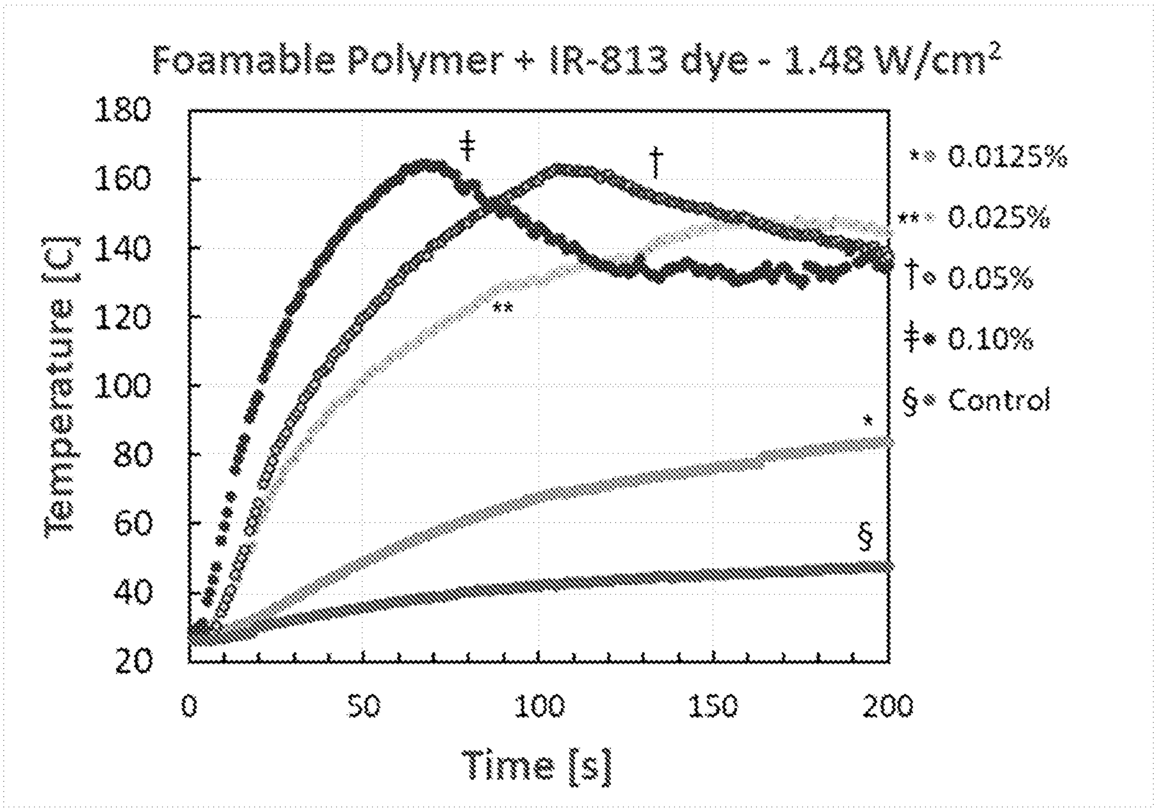
Foamable Polymer + IR-813 dye - 1.48 W/cm²
Temperature [C]
Time [s]
180
160
140
120
100
80
60
40
20
0
50
100
150
200
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 7

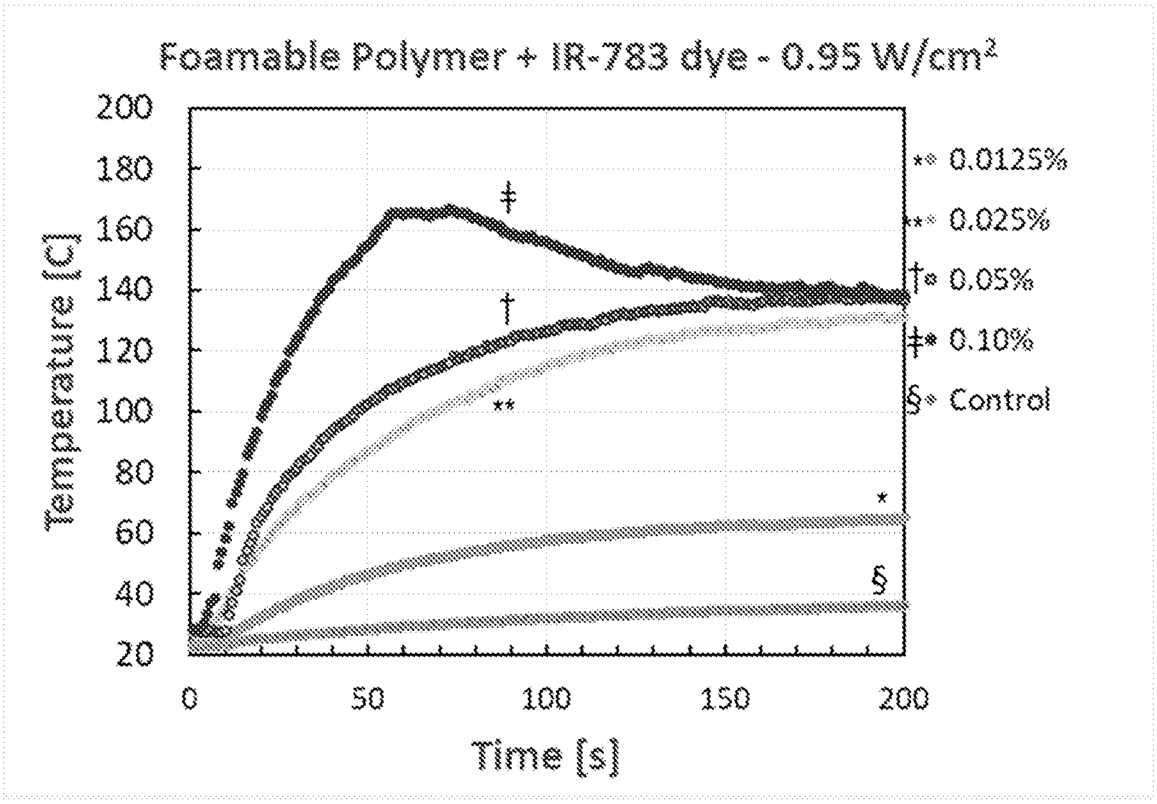
Foamable Polymer + IR-783 dye - 0.95 W/cm²
Temperature [C]
Time [s]
200
180
160
140
120
100
80
60
40
20
0
50
100
150
200
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 8

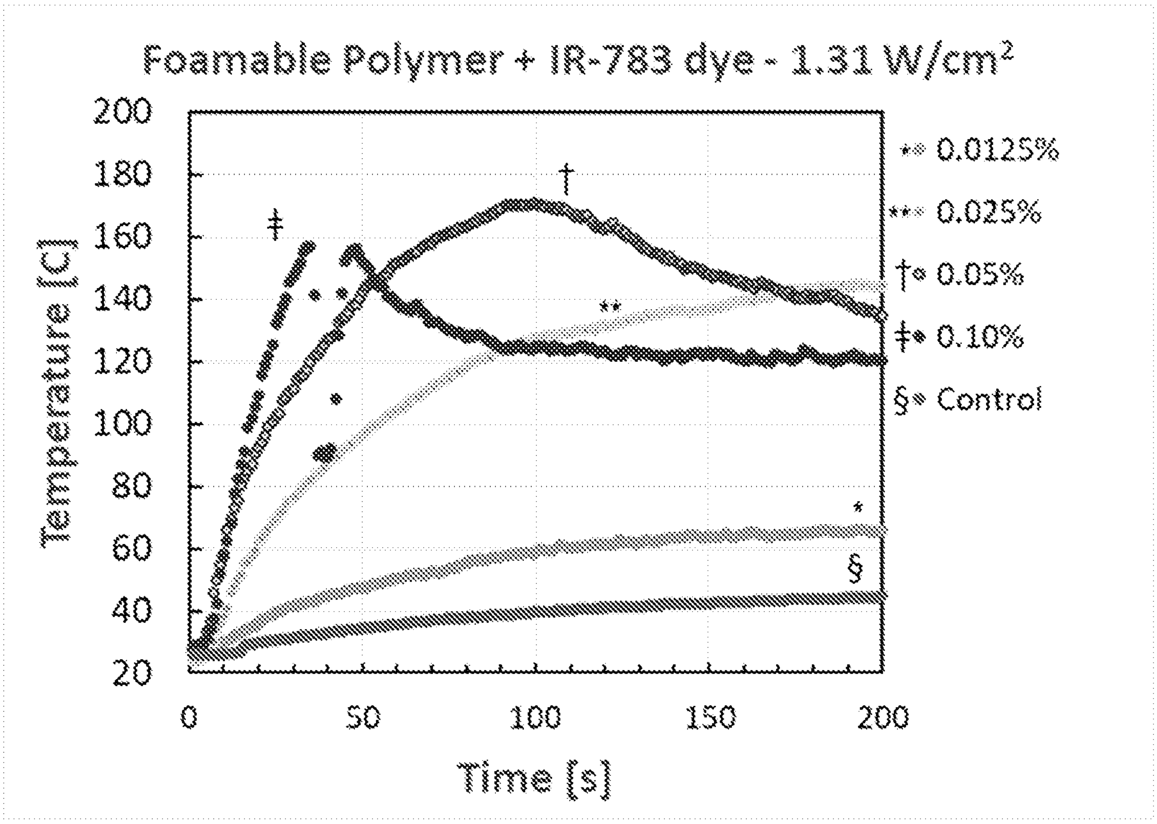
Foamable Polymer + IR-783 dye - 1.31 W/cm^2
Temperature [C]
200
180
160
140
120
100
80
60
40
20
0
50
100
150
200
Time [s]
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 9

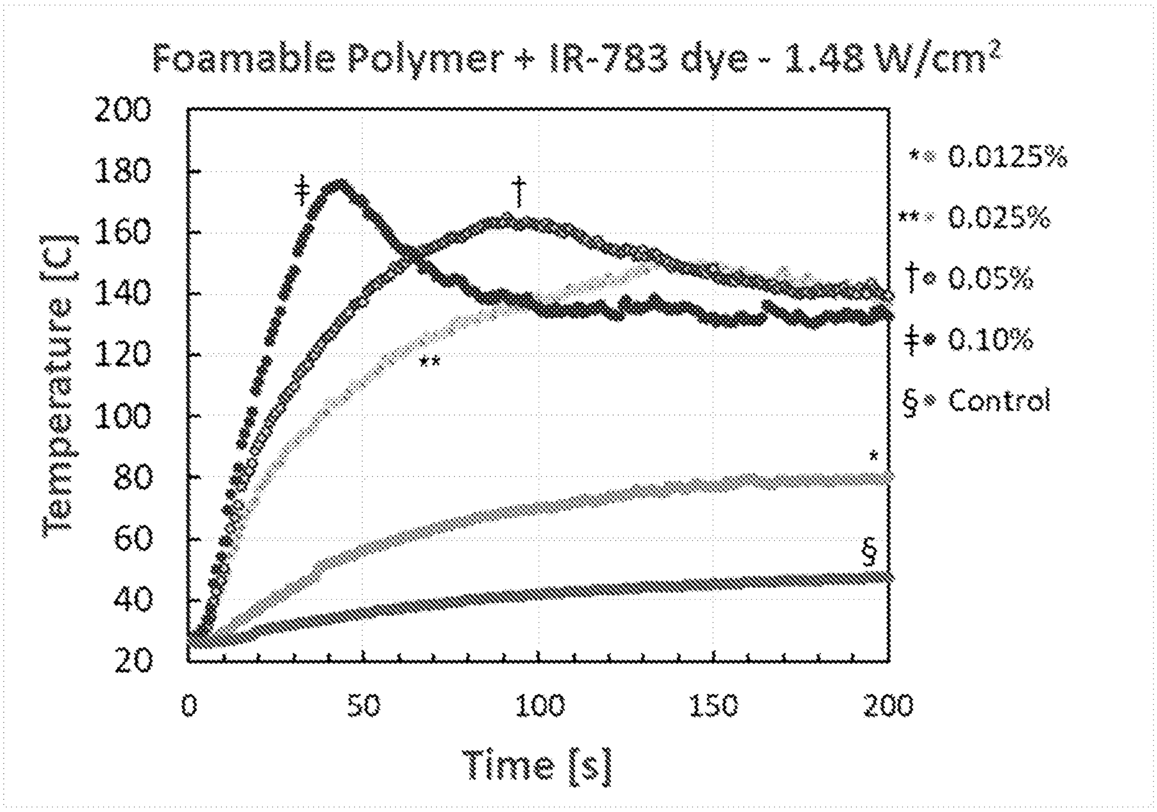
Foamable Polymer + IR-783 dye - 1.48 W/cm^2
Temperature [C]
200
180
160
140
120
100
80
60
40
20
0
50
100
150
200
Time [s]
‡
†
**
*
§
* 0.0125%
** 0.025%
† 0.05%
‡ 0.10%
§ Control

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/056301

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08F 220/02*** (2024.01); ***C08F 220/04*** (2024.01); *C08F 220/06* (2024.01)
CPC: ***C08F 220/02; C08F 220/04;*** *C08F 220/06*

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	EP 3272518 B1 (WASHIO ET AL.) 11 May 2022 (11.05.2022) entire document especially para [0025], [0068], [0093], [0048]-[0049], [0212]-[0213], [0057], [0235]	1-2, 7/1, 7/2
A	US 2016/0304752 A1 (RIKEN TECHNOS CORPORATION) 20 October 2016 (20.10.2016) entire document	1-2, 7/1, 7/2
A	US 6,206,550 B1 (FUKUSHIMA ET AL.) 27 March 2001 (27.03.2001) entire document	1-2, 7/1, 7/2
A	US 2012/0251831 A1 (OKAYASU ET AL.) 04 October 2012 (04.10.2012) entire document	1-2, 7/1, 7/2
A	US 2016/0159995 A1 (RIKEN TECHNOS CORPORATION) 09 June 2016 (09.06.2016) entire document	1-2, 7/1, 7/2
A	WO 2023/012268 A1 (ROHM GMBH) 09 February 2023 (09.02.2023) entire document	1-2, 7/1, 7/2

☐ 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	"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
"D" document cited by the applicant in the international application	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search **13 December 2024 (13.12.2024)**	Date of mailing of the international search report **20 February 2025 (20.02.2025)**
Name and mailing address of the ISA/US **COMMISSIONER FOR PATENTS** **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA** Facsimile No. **571-273-8300**	Authorized officer **KARI RODRIQUEZ** Telephone No. **PCT Help Desk: 571-272-4300**

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.: **8-106**
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:

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.

Group I: Claims 1-2, 7/1, and 7/2 are directed towards a method of preparing a poly(meth)acrylimide, the method comprising the steps of: (a) irradiating a reaction mixture with radiation to form a solid layer of a precursor polymer, the radiation comprising actinic radiation, wherein: at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules; the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and at the end of the irradiation, the reaction mixture has a percent conversion of at least 40%; (b) imidizing at least a section of the layer of the precursor polymer to generate the poly(meth)acrylimide.

Group II: Claims 3-6 and 7/(3-6) are directed towards a method of preparing a poly(meth)acrylimide, the method comprising the steps of: (a) irradiating a reaction mixture with radiation comprising actinic radiation, wherein: at the start of the irradiation, the reaction mixture comprises a plurality of monomer molecules, a near-infrared dye, and an initiator; at the start of the irradiation, a percent conversion of the reaction mixture is less than 10%; the actinic radiation comprises electromagnetic radiation having a wavelength of greater than or equal to 100 nm and less than or equal to 2500 nm and/or comprises electron beam radiation; and at the end of the irradiation, the reaction mixture comprises liquid in an amount of less than 20%; (b) imidizing at least a portion of the precursor polymer to generate the poly(meth)acrylimide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/056301

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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.: **1-2, 7/1, 7/2**

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.