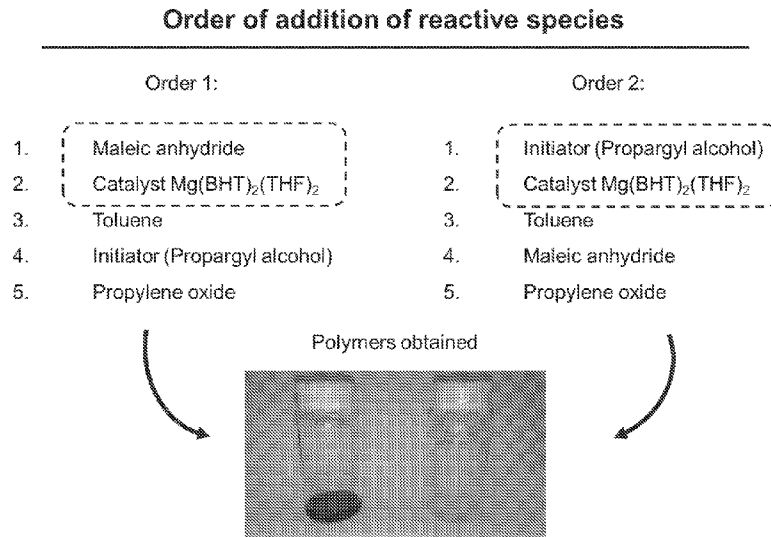




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(54) Title: POLY(PROPYLENE FUMARATE)-BASED COPOLYMERS FOR 3D PRINTING APPLICATIONS

**FIG. 1**

(57) **Abstract:** In various embodiments, the present invention is directed to a PPF-based copolymer for 3D printing applications and methods for its making and use. These copolymers have a viscosity in a printable viscosity range and allow light transmittance at curing wavelengths. In various embodiments, a lower viscosity copolymers are obtained by substitution of a portion of maleic anhydride with succinic anhydride and then forming a poly(propylene fumarate-co-succinate) copolymer by the copolymerization of maleic anhydride and succinic anhydride with propylene oxide via $\text{Mg}(\text{BHT})_2(\text{THF})_2$ catalyzed ring opening copolymerization (ROCOP). Because of their lower viscosities, these copolymers require less, if any, diethyl fumarate (DEF) to prepare the 3D printing resin, while the mechanical properties can still be adjusted as with a PPF polymer prepared without the succinic anhydride.



SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
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POLY(PROPYLENE FUMARATE)-BASED COPOLYMERS FOR 3D PRINTING APPLICATIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. provisional patent application serial number 62/697,613 entitled “Poly(Propylene Fumarate)-Based Copolymers for 3D Printing Applications,” filed July 13, 2019, and incorporated herein by reference in its entirety.

NAMES OF THE PARTIES TO A JOINT RESEARCH AGREEMENT

[0002] The present application stems from work done pursuant to a Joint Research Agreement between The University of Akron of Akron, Ohio and 3D BioActives, LLC of Akron, Ohio.

FIELD OF THE INVENTION

[0003] One or more embodiments of the present invention relates to a 3D printable and degradable polymer for use in medical devices and applications. In certain embodiments, the present invention relates to poly(propylene fumarate)(PPF)-based polymers and copolymers for use as medical devices or tissue scaffolds that have a viscosity in a 3D printable viscosity range and allow transmittance of the light at photochemically curing wavelengths.

BACKGROUND OF THE INVENTION

[0004] Additive manufacturing, also known as 3D printing, has enabled a new frontier for regenerative medicine due to its ability to fabricate patient and defect specific devices precisely. In particular continuous digital light processing (cDLP) photochemical printing builds all pixels in one layer simultaneously, therefore the build time is much faster than other additive manufacturing methods. In addition to photopolymers, slurry resins that containing fillers, such as nanoparticles or ceramics,

can be processed through photo stereolithography, which make cDLP a promising technique for a stress bearing applications.

[0005] Poly(propylene fumarate)(PPF) is a resorbable polyester that forms fumaric acid and propylene glycol after degradation *in vivo*, which are readily excreted from the body. It has been extensively studied for medical device applications, such as drug delivery, blood vessel engineering, nerve grafts, cartilage and bone tissue scaffolds. PPF has an unsaturated double bond in its polymer back bone, which can be crosslinked post-polymerization in photochemical reactions. Oligomeric poly(propylene fumarate)(PPF) is 3D printable through stereolithographic processes and has been found to be a promising material for the construction of medical devices and 3D scaffolds for bone regeneration application using stereolithographic methods, such as cDLP (continuous digital light processing) or liquid crystal display-based printing.

[0006] When first introduced in 1994, PPF was synthesized by step-growth polymerization with diethyl fumarate and propylene glycol. However, due to intrinsic limitations of step growth polymerization, the molecular mass of PPF is hard to control using these methods. Targeting oligomers (degree of polymerization (DP) < 20) resulted in relatively low conversion, starting material contamination and broad molecular mass distributions ($\bar{D}_m$). More recently, techniques for production of PPF by ring-opening copolymerization (ROCOP) of maleic anhydride and propylene oxide have been reported. Initially, these methods yielded PPF with a narrow $\bar{D}_m$, but that suffered from a low conversion and homopolymerization of the propylene oxide, producing byproducts not easily degraded in the body. By about 2011, methods for production of PPF using a two-step process in which a well-defined ROCOP method yielded poly(propylene maleate) (PPM) intermediate in a first step and then, in a second reaction the PPM intermediate was isomerized to produce the PPF. These methods produced a PPF Polymer with a high conversion with a narrow $\bar{D}_m$ but used a cobalt catalyst that raised cytocompatibility concerns. More recently, PPF has been successfully synthesized via ROCOP using $\text{Mg}(\text{BHT})_2(\text{THF})_2$ as the catalyst. This methods resulted in a well-defined molecular mass PPF, having a narrow $\bar{D}_m$ and high end group fidelity at high conversion.

[0007] Due to the decreasing solubility with increasing chain length, PPF is a solid when its molecular mass is greater than 4000 Da. Viscosity of PPF is directly correlated to chain length and increases with increasing degree of polymerization (DP). The viscosity of pure PPF (~400 Da) at 40 °C is above 24,000 cP, which is much higher than the ideal viscosity for cDLP of between 2 cP and 200 cP. In general, the resin viscosity has to be less than 5 Pa sec to print features with 200 μ m struts and 400 μ m pores using cDLP. Consequently, only low molecular mass (< 3000 Da) oligomers are suitable for cDLP and the high viscosity of PPF limits it from being used its pure polymeric form for most 3D printing applications.

[0008] To take advantage of cDLP, the 3D printing material is formulated as a low viscosity resin that is typically composed of photosensitive oligomers, diluent and photoinitiators. In photochemistry-based 3D printing resins using PPF, diethyl fumarate (DEF) or another solvent is usually added to PPF oligomer as a diluent to reduce its viscosity and facilitate crosslinking. Historically, PPF resins have contained DEF as a reactive diluent at up to 50 wt. % to reach a printable viscosity. DEF not only acts as a solvent but is also incorporated into the 3D printing reaction through its double bond and, depending upon the amount used, the DEF is incorporated into the network and can affect the mechanical properties of 3D printed scaffold. Also, because DEF can be toxic, unreacted, residual DEF must be removed from the cured scaffolds before they can be used in medical devices or applications. By reducing the viscosity of PPF, the amount of DEF required to make the 3D printable resin is also reduced.

[0009] Because the viscosity of the PPF is closely related to its degree of polymerization, it is important to control degree of polymerization and dispersity of PPF. Ring opening polymerization (ROP) and ring opening copolymerization (ROROP) are known to be an appropriate method to synthesize polymers with precise molecular mass and narrow molecular mass distributions. ROP and ROCOP require a catalyst and $\text{Mg}(\text{BHT})_2(\text{THF})_2$ has been found to be a good catalyst as it affords high activity (more than 95% conversion with less than 1.5 dispersity). However, the PPF that is polymerized with $\text{Mg}(\text{BHT})_2(\text{THF})_2$ catalyst has also been found in some cases to have high absorbance at the wavelength in which 3D printing is conducted, which can

increases 3D printing times. The high absorbance of these PPF polymers can cause many problems, such as prolonging the production time, limiting production the amount, creating the potential for failure of 3D printing during manufacturing, creating the need for higher light power source, and increasing the consumption of energy. Moreover, since the wavelength of light used for 3D printing depends on the manufacturer of 3D printing machine, production of a PPF polymer that has a lower absorbance along the entire possible wavelength range is strongly desired.

[0010] What is needed in the art is a PPF polymer for use in 3D printing having a viscosity in a printable viscosity range and a low absorbance at curing wavelengths.

SUMMARY OF THE INVENTION

[0011] In various embodiments, the present invention is directed to a PPF based polymers and copolymers for 3D printing applications (and methods for is making and use) that have a viscosity in a 3D printable viscosity range and low absorbance values at curing wavelengths. As set forth above, the viscosity of the PPF is closely related to its degree of polymerization, so the degree of polymerization and dispersity of the PPF are carefully controlled. In various embodiments of the present invention, this is accomplished by obtaining lower viscosity of the PPF by the substitution of a portion of maleic anhydride with succinic anhydride, and then forming a PPF-based 3D printable polymer by the copolymerization of maleic anhydride and succinic anhydride with propylene oxide using $\text{Mg}(\text{BHT})_2(\text{THF})_2$ catalyzed ROP and ROCOP. Moreover, it has been found that by altering the order of addition of the reactive species of the $\text{Mg}(\text{BHT})_2(\text{THF})_2$ catalyzed ROP and ROCOP reactions, PPF-based 3D printable polymer having lower absorbance values at curing wavelengths can be produced. The copolymers of the present invention have lower viscosities and lower absorbance than known PPM and PPF polymers, while maintaining 3D printability. Further, because the PPF based polymers and copolymers of the present invention have lower viscosities, less diethyl fumarate (DEF) is required to prepare the 3D printing resin, while the mechanical properties can still be adjusted in the same ways as a PPF polymer prepared by ROP or ROCOP without the succinic anhydride. Moreover, the curing time of 3D printing for

these PFF-based polymers is reduced compared with the PPF that are prepared without succinic anhydride using $\text{Mg}(\text{BHT})_2(\text{THF})_2$ as catalyst.

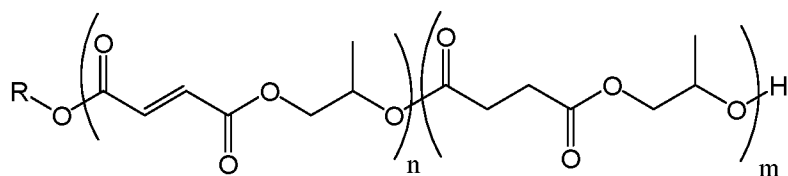
[0012] In a first aspect, the present invention is directed to a polymer composition comprising the one or more isomerized residues of maleic anhydride monomer, one or more residue of succinic anhydride monomer and one or more residues of propylene oxide monomer. In one or more embodiments, the polymer composition will comprise from about 1 to about 30 mole percent, preferably from about 1 to about 20 mole percent, and more preferably from about 1 to about 10 mole percent succinic anhydride residues. In some embodiments, the polymer composition will comprise about 50 mole percent propylene oxide residues.

[0013] In one or more embodiments, the polymer composition of the present invention a degree of polymerization (DP) of from about 5 to about 100, preferably from about 5 to about 50, and more preferably from about 5 to about 10. In one or more embodiments, the polymer composition of the present invention includes any one or more of the above referenced embodiments of the first aspect of the present invention having a number average molecular weight (M_n) of from about 0.5 kDa to about 100 kDa, preferably from about 0.5 kDa to about 50 kDa, and more preferably from about 0.5 kDa to about 5 kDa, as measured by size exclusion chromatography (SEC) or gel permeation chromatography (GPC). In one or more embodiments, the polymer composition of the present invention includes any one or more of the above referenced embodiments of the first aspect of the present invention having a mass distribution ($\mathcal{D}_m$) of from about 1 to about 2, preferably from about 1 to about 1.5, and more preferably from about 1 to about 1.2.

[0014] In one or more embodiments, the polymer composition of the present invention includes any one or more of the above referenced embodiments of the first aspect of the present invention having a zero sheer viscosity of from about 500 Pa·s to about 10,000 Pa·s, preferably from about 1000 Pa·s to about 7,000 Pa·s, and more preferably from about 1000 Pa·s to about 5000 Pa·s, as measured by a rheometer. In one or more embodiments, the polymer composition of the present invention includes any one or more of the above referenced embodiments of the first aspect of the present

invention having a zero shear viscosity of from about 1.5 Pa·s to about 2.5 Pa·s, preferably from about 1.7 Pa·s to about 2.4 Pa·s, and more preferably from about 1.8 Pa·s to about 2.2 Pa·s, as measured by a rheometer when diluted with 30 weight percent DEF. In one or more embodiments, the polymer composition of the present invention includes any one or more of the above referenced embodiments of the first aspect of the present invention having an absorbance at wavelengths from about 305 nm to about 405 nm of from about 0.001 to about 0.3, preferably from about 0.001 to about 0.2, and more preferably from about 0.001 to about 0.1, as measured by a UV-Visible spectrometer.

[0015] In one or more embodiments, the polymer composition of the present invention includes any one or more of the above referenced embodiments of the first aspect of the present invention having the formula:



where R is alkyl, alkene, alkyne or aromatic group; n is a mole fraction from about 0.50 to about 0.99 and m is a mole fraction from about 0.01 to about 0.50.

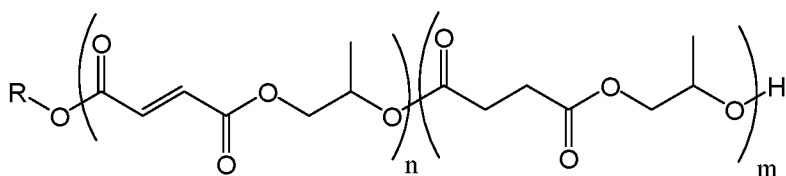
[0016] In a second aspect, the present invention is directed to a polymer for use in 3D printable resins comprising the isomerized reaction product of maleic anhydride, succinic anhydride and propylene oxide. In one or more embodiments, the polymer for use in 3D printable resins will comprise from about 1 to about 30 mole percent, preferably from about 1 to about 20 mole percent, and more preferably from about 1 to about 10 mole percent succinic anhydride residues. In some embodiments, the polymer for use in 3D printable resins comprises about 50 mole percent propylene oxide residues.

[0017] In one or more embodiments, the polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having a degree of polymerization (DP) of from about 5 to about 100, preferably from about 5 to about 50, and more preferably from about 5 to about 10. In one or more embodiments, the polymer for use in 3D

printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having a number average molecular mass (M_n) of about 0.5 kDa to about 100 kDa, preferably from about 0.5 kDa to about 50 kDa, and more preferably from about 0.5 kDa to about 5 kDa, as measured by size exclusion chromatography (SEC) or gel permeation chromatography (GPC). In one or more embodiments, the polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having a mass distribution (D_m) of from about 1 to about 2, preferably from about 1 to about 1.5, and more preferably from about 1 to about 1.2.

[0018] In one or more embodiments, the polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having a zero shear viscosity of from about 500 Pa·s to about 10,000 Pa·s, preferably from about 1000 Pa·s to about 7,000 Pa·s, and more preferably from about 1000 Pa·s to about 5000 Pa·s, as measured by a rheometer. In one or more embodiments, the polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having a zero shear viscosity of from about 1.5 Pa·s to about 2.5 Pa·s, preferably from about 1.7 Pa·s to about 2.4 Pa·s, and more preferably from about 1.8 Pa·s to about 2.2 Pa·s, as measured by a rheometer when diluted with 30 weight percent DEF. In one or more embodiments, the polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having an absorbance at wavelengths from about 305 nm to about 405 nm of from about 0.001 to about 0.3, preferably from about 0.001 to about 0.2, and more preferably from about 0.001 to about 0.1, as measured by a UV-Visible spectrometer.

[0019] In one or more embodiments, the polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the second aspect of the present invention having the formula:



where R is alkyl, alkene, alkyne or aromatic group; n is a mole fraction from about 0.50 to about 0.99 and m is a mole fraction from about 0.01 to about 0.50.

[0020] In a third aspect, the present invention is directed to a method of making a polymer for use in 3D printable resins comprising: reacting maleic anhydride, succinic anhydride and propylene oxide and an initiating alcohol in the presence of a magnesium catalyst to form a poly(propylene maleate-co-succinate) copolymer intermediate having a maleic anhydride residue containing a *cis* double bond; and isomerizing the *cis* double bond in the maleic anhydride residue by reacting the poly(maleic anhydride-co-succinic anhydride-co-propylene oxide) polymer intermediate to form a poly(propylene fumarate-co-succinate) copolymer. In one or more of these embodiments, the method further comprises washing the solution with a buffer solution to remove any residual amine, and drying the product to recover the poly(propylene fumarate-co-succinate) copolymer.

[0021] In one or more embodiments, the initiating alcohol is selected from the group consisting of benzyl alcohol, propargyl alcohol, 4-hydroxybutan-2-one, 5-norbonen-2-ol, butanone, ethyl alcohol, isopropyl alcohol, tertiary butyl alcohol, and combinations thereof. In various embodiments, the magnesium catalyst is $\text{Mg}(\text{BHT})_2(\text{THF})_2$.

[0022] In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the step of reacting comprises: placing an initiating alcohol and $\text{Mg}(\text{BHT})_2(\text{THF})_2$ in a suitable sealed reaction vessel and then adding propylene oxide, maleic anhydride, succinic anhydride and a suitable solvent; heating the combination until substantially all of the maleic anhydride, succinic anhydride and propylene oxide have reacted to form a poly(propylene maleate-co-succinate) copolymer intermediate; precipitating the poly(propylene maleate-co-succinate) copolymer intermediate into an excess of a non-

solvent for the poly(propylene maleate-co-succinate) copolymer intermediate; and drying the poly(propylene maleate-co-succinate) copolymer intermediate to remove remaining solvent. In one or more embodiments, the suitable solvent in the step of combing is selected from toluene, hexane, and combinations thereof.

[0023] In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the molar ratio of maleic anhydride to succinic anhydride in the step of combining is from about 100:1 to about 1:1, preferably from about 50:1 to about 1:1, and more preferably from about 2:1 to about 1:1. In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the step of heating comprises heating the combination to a temperature of from about 40°C to about 80°C for from about 1 hours to about 48 hours or until substantially all of the maleic anhydride, succinic anhydride, and propylene oxide monomers have reacted.

[0024] In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the step of precipitating comprises combing the product with an excess of diethyl ether to cause the poly(propylene maleate-co-succinate) copolymer intermediate to precipitate out of solution. In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the step of drying is performed by vacuum evaporation.

[0025] In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the step of isomerizing comprises: dissolving the poly(propylene maleate-co-succinate) copolymer intermediate in a suitable solvent; and adding diethylamine to the solution and heating it to a reflux temperature under an inert atmosphere to produce the poly(propylene

fumarate-co-succinate) copolymer. In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the suitable solvent for the poly(propylene maleate-co-succinate) copolymer intermediate is selected from the group consisting of chloroform, dichloromethane, and combinations thereof. In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the solution is heated to a reflux temperature under an inert atmosphere for from about 1 to about 48 hours or until substantially all of poly(propylene maleate-co-succinate) copolymer intermediate has isomerized.

[0026] In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the buffer solution in the step of washing is a phosphate buffer solution. In one or more embodiments, the method for making a polymer for use in 3D printable resins of the present invention includes any one or more of the above referenced embodiments of the third aspect of the present invention wherein the step of drying is performed by vacuum evaporation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures in which:

[0028] FIG. 1 is an image and associated description showing poly(propylene fumarate-co-succinate) copolymers made with different orders of addition for the reactive species;

[0029] FIGS. 2A-C are a ^1H NMR spectrum of poly(propylene maleate-co-propylene succinate) with 10 mol% succinate and a degree of polymerization (DP) of 10 initiated with propargyl alcohol (300 MHz, 303 K, CHCl_3) (FIG. 2A); a ^1H NMR spectrum of the

corresponding poly(propylene fumarate-co-propylene succinate) following isomerization (FIG. 2B); and a Diffusion Ordered Spectroscopy (DOSY) NMR (500 MHz, 303 K, CHCl₃) spectrum of poly(propylene maleate-co-propylene succinate) indicating single diffusing species without homopolymer contamination (FIG. 2C);

[0030] FIG. 3 is a MALDI-ToF MS spectrum for the *cis*-copolymer (poly(propylene maleate-co-propylene succinate) polymer intermediate with an insert enlarging the area from about 1450 Da to about 1700 Da showing an observed mass of 156 Da between two adjacent peaks that revealed that the major repeat unit was propylene maleate and a highest peak that is 2 Da from the initial monoisotopic mass, which indicates a repeating unit 158 Da that corresponds to propylene succinate unit is present in polymer chain;

[0031] FIG. 4 is a matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) plot of propargyl alcohol initiated poly(propylene maleate-co-propylene succinate) of DP 10 with 10 mol% succinate;

[0032] FIGS. 5A-B are a kinetic plot for the copolymerization of maleic anhydride, succinic anhydride and propylene oxide, conducted at 80 °C in toluene with [MAn]₀:[SAn]₀:[PO]₀:[PA]₀: [Cat]₀ = 80:20:100:10:1, total monomer concentration = 7 M (FIG. 5A) and a graph showing changes in number-average molecular mass (M_n) and D_M over increasing monomer conversion for the same copolymerization, determined by SEC against poly(styrene) standards (FIG. 5B);

[0033] FIGS. 6 is a quantitative ¹³C NMR of DP10 20% copolymer;

[0034] FIGS. 7 MALDI-ToF MS of the *trans*-copolymer;

[0035] FIGS. 8A-B are a plot showing complex viscosity data for poly(propylene fumarate) resins (50 wt% DEF) possessing a degree of polymerization of 10 (open symbols) and 20 (solid symbols) repeat units without succinate (squares) and with approximately 10 (circles) and 20 mole (diamonds) percent succinate incorporation, respectively (FIG. 8A) and a plot showing viscosity of uncrosslinked resin formulations possessing different polymer/DEF weight ratios at 25 °C (FIG. 8B);

[0036] FIG. 9 is a graph showing complex viscosity data of 80 wt% and 100 wt% of poly(propylene fumarate) resins without succinate (square) and 20 mole (diamond) percent succinate incorporation at different temperature;

[0037] FIGS. 10A-B are a graph showing stress/strain curves for 3D printed tensile bars with with 50 wt%, 60 wt% and 70 wt% copolymer resins of DP10, 20% copolymer (FIG. 10A) and a plot showing tensile properties measurement of 3D printed tensile bars with 50 wt%, 60 wt% and 70 wt% copolymer resins for 10 mole% (open symbols) and 20 mole% (solid symbols) succinate copolymer with degree of polymerization of 10 (FIG. 10B);

[0038] FIGS. 11 is a graph showing swelling test results of 3D printed tensile bars for 10 mole% and 20 mole% succinate copolymer with 50 wt%, 60 wt% and 70 wt% copolymer in the printed resin;

[0039] FIG. 12 is a ^1H NMR spectrum of DP 10 PPM;

[0040] FIG. 13 is a ^1H NMR spectrum of DP 20 PPM;

[0041] FIG. 14 is a ^1H NMR spectrum of DP 20, 5 mol% succinic anhydride feed copolymer;

[0042] FIG. 15 is a ^1H NMR spectrum of DP 20, 10 mol% succinic anhydride feed copolymer;

[0043] FIG. 16 is a ^1H NMR spectrum of DP 20, 20 mol% succinic anhydride feed copolymer;

[0044] FIG. 17 is a ^1H NMR spectrum of DP 20, 30 mol% succinic anhydride feed copolymer;

[0045] FIG. 18 is a ^1H NMR spectrum of DP 20, 50 mol% succinic anhydride feed copolymer;

[0046] FIG. 19 is a ^1H NMR spectrum of DP 20, 100 mol% succinic anhydride feed copolymer;

[0047] FIG. 20 is a ^1H NMR spectrum of DP 10, 10 mol% succinic anhydride feed copolymer;

[0048] FIG. 21 is a ^1H NMR spectrum of DP 10, 20 mol% succinic anhydride feed copolymer;

[0049] FIG. 22 is a ^1H NMR spectrum of DP 10 poly(propylene fumarate) (PPF);

[0050] FIG. 23 is a ^1H NMR spectrum of DP 20 poly(propylene fumarate) (PPF);

[0051] FIG. 24 is a ^1H NMR spectrum of DP 10 and 10 mol% succinic anhydride feed copolymer after isomerization;

[0052] FIG. 25 is a ^1H NMR spectrum of DP 10 and 20 mol% succinic anhydride feed copolymer after isomerization;

[0053] FIG. 26 SEC chromatograph for DP10, 20% succinic anhydride feed copolymer;

[0054] FIG. 27 is a ^1H NMR spectrum of DP 20 and 10 mol% succinic anhydride feed copolymer after isomerization;

[0055] FIG. 28 is a ^1H NMR spectrum of DP 20 and 20 mol% succinic anhydride feed copolymer after isomerization;

[0056] FIG. 29 is a graph showing complex viscosity data obtained for isomerized copolymers with DP 10 and DP 20 and 0, 10 or 20 mol% succinate units in a 50% solution (by weight) DEF solution using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode;

[0057] FIG. 30 is a graphs showing viscosity data for DEF solutions containing different concentrations of isomerized copolymers according to various embodiments of the present invention.

[0058] FIG. 31 is a ^1H NMR spectrum of DP 13 and 11 mol% succinic anhydride feed copolymer after isomerization;

[0059] FIG. 32 is a ^1H NMR spectrum of DP 19 and 9 mol% succinic anhydride feed copolymer after isomerization.

[0060] FIGS. 33A-D are kinetic plots for the copolymerization of maleic anhydride and propylene oxide, conducted at 80 °C in toluene with $[\text{MAN}]_0 : [\text{PO}]_0 : [\text{PrOH}]_0 : [\text{Cat.}]_0 = 20 : 20 : 1 : 0.2$, total initial monomer concentration of 7 M with 2 different addition orders of addition of reactive species where FIG. 33A is a graph showing the evolution of $\ln([M_0]/[M_t])$ with time (triangle: Catalyst+Man and circles: Catalyst+alcohol); FIG. 33B is a graph showing the evolution of conversion with time (triangles: Catalyst+Man and circles: Catalyst+alcohol) ; FIG. 33C is a graph showing the evolution of molar mass and dispersity with the conversion for the Catalyst+Man system; and FIG. 33D is a graph showing the evolution of molar mass and dispersity with

the conversion for the Catalyst+alcohol system. Calculations based on ^1H NMR in CDCl_3 and dispersity values determined by SEC in DMF (polystyrene calibration); and

[0061] FIGS. 34A-B are graphs showing the evolution of the complex viscosity with the angular frequency of the PPF:DEF resins made using with 2 different orders of addition for reactive species, namely a dark PPF where the maleic anhydride is added before the initiating alcohol (FIG. 34A) and a light PPF where the initiating alcohol is added before the maleic anhydride and/or succinic anhydride (FIG. 34B).

DETAILED DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

[0062] In various embodiments, the present invention is directed to a PPF-based copolymer for 3D printing applications and methods for its making and use. These copolymers have a viscosity in a printable viscosity range and allow light transmittance at curing wavelengths. Viscosity is closely related with degree of polymerization and stoichiometry of the monomers, so the degree of polymerization and molecular mass distribution of the PPF or PPF-based copolymer must be carefully controlled. In various embodiments of the present invention, lower viscosity of the PPF is obtained by substitution of a portion of the maleic anhydride with succinic anhydride and then forming a poly(propylene fumarate-co-succinate) copolymer by the copolymerization of maleic anhydride and succinic anhydride with propylene oxide via $\text{Mg}(\text{BHT})_2(\text{THF})_2$ catalyzed ROCOP. While not wanting to be bound by theory, it is believed that addition of the succinic anhydride reduces the viscosity of PPF because it alters the chain-chain interaction of the polymer by modifying the stoichiometry or chain architecture. Further, because these PPF-based copolymers have lower viscosities, less diethyl fumarate (DEF) is required to prepare the 3D printing resin, while the mechanical properties can still be adjusted in the same manner as a PPF polymer prepared without the succinic anhydride.

[0063] Moreover, as set forth above, by altering the order of addition of the reactive species of the $\text{Mg}(\text{BHT})_2(\text{THF})_2$ catalyzed ROP and ROCOP reactions, PPF-based 3D printable polymer having lower absorbance values at curing wavelengths can be produced. It has been found that addition of the maleic anhydride and/or succinic anhydride before initiating alcohol produces a polymer with a relatively high absorbance

(generally greater than 0.5). However, if the initiating alcohol is added before the maleic anhydride and succinic anhydride, a PPF-based 3D printable polymer having much lower absorbance (generally less than 0.3) at curing wavelengths may be produced. Moreover, the curing time of 3D printing for these PPF-based polymers is reduced compared with the PPF that are prepared without succinic anhydride using $\text{Mg}(\text{BHT})_2(\text{THF})_2$ as catalyst.

[0064] The following terms may have meanings ascribed to them below, unless specified otherwise. As used herein, the terms "comprising" "to comprise" and the like do not exclude the presence of further elements or steps in addition to those listed in a claim. Similarly, the terms "a," "an" or "the" before an element or feature does not exclude the presence of a plurality of these elements or features, unless the context clearly dictates otherwise.

[0065] Unless specifically stated or obvious from context, as used herein, the term "about" is understood as within a range of normal tolerance in the art, for example within 2 standard deviations of the mean. "About" can be understood as within 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, 0.5%, 0.1%, 0.05%, or 0.01% of the stated value. Unless otherwise clear from context, all numerical values provided herein in the specification and the claim can be modified by the term "about."

[0066] It should be also understood that the ranges provided herein are a shorthand for all of the values within the range and, further, that the individual range values presented herein can be combined to form additional non-disclosed ranges. For example, a range of 1 to 50 is understood to include any number, combination of numbers, or sub-range from the group consisting of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, or 50.

[0067] In a first aspect, the present invention is directed to a PPF-based 3D printable polymer composition comprising a poly(propylene fumarate-co-succinate) copolymer. In one or more embodiments, the PPF-based 3D printable polymer composition of the present invention will comprise the isomerized residues of a maleic anhydride monomer, residues of succinic anhydride monomer and residues of a propylene oxide. As used

herein, the term “residue(s)” is used to refer generally to the portion of a monomer or other chemical unit that has been incorporated into a polymer or other large molecule. As follows, the terms “residues of succinic anhydride monomer,” “residues of succinic anhydride” and “succinic anhydride residue(s)” are all used herein to refer to the portion(s) of succinic anhydride monomer and the terms “residues of propylene oxide monomer,” “residues of propylene oxide” and “propylene oxide residue(s)” are all used herein to refer to the portion(s) of propylene oxide monomer incorporated into the poly(propylene fumarate-co-succinate) copolymer. Similarly, the terms “isomerized residue of a maleic anhydride monomer,” “isomerized residues of maleic anhydride monomer,” “isomerized residue of a maleic anhydride,” “isomerized residues of maleic anhydride,” and “isomerized maleic anhydride residue(s)” are used interchangeably to refer to residue(s) of the maleic anhydride monomer incorporated into the poly(propylene fumarate-co-succinate) copolymer of the present invention in which the double bond has subsequently been isomerized from the *cis* (maleate) configuration to the *trans* (fumarate) configuration during formation of the poly(propylene fumarate-co-succinate) copolymer from the poly(propylene maleate-co-succinate) copolymer intermediate, as described below.

[0068] As will be apparent, the succinic anhydride molecule closely resembles the maleic anhydride, but lacks the photopolymerizable double bond. It has been found that succinic anhydride will polymerize with propylene oxide in much the same way as maleic anhydride, but produces copolymers having a lower viscosity and absorption than comparable polymers made with maleic anhydride. However, the lack of a double bond in the backbone of the succinic anhydride monomer ensures that it will not be crosslinked and does not need isomerization.

[0069] It has been found, however, that by replacing some portion of the maleic anhydride used in the synthesis of PPF by ROCOP with succinic anhydride, it is possible to produce a PPF-based polymer (poly(propylene fumarate-co-succinate)) having a lower viscosity and a lower adsorption, while still maintaining the good mechanical properties of pure PPF. In some of these embodiments, the copolymer composition of the present invention will comprise from about 1 to about 30 mole percent, preferably from about 1

to about 20 mole percent, and more preferably from about 1 to about 10 mole percent succinic anhydride residues. In some embodiments, the copolymer composition of the present invention will comprise from about 1 to about 25 mole percent, in other embodiments, from about 1 to about 15 mole percent, in other embodiments, from about 1 to about 5 mole percent, in other embodiments, from about 5 to about 30 mole percent, in other embodiments, from about 10 to about 30 mole percent, in other embodiments, from about 15 to about 30 mole percent, in other embodiments, from about 20 to about 30 mole percent, and in other embodiments, from about 25 to about 30 mole percent. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges. As will be apparent, propylene oxide residues will comprise about 50 mole percent of these copolymers, with the balance being isomerized residues of maleic anhydride and residues of the initiating alcohols.

[0070] As set forth above, the degree of polymerization and dispersity of the PPF must be carefully controlled to obtain polymers having the desired viscosity. In one or more embodiments, the polymer composition of the present invention will have a degree of polymerization (DP) of from about 5 to about 100, preferably from about 5 to about 50, and more preferably from about 5 to about 10. In some embodiments, the polymer composition of the present invention will have a degree of polymerization (DP) of from about 1 to about 200, in other embodiments, from about 1 to about 100, in other embodiments, from about 1 to about 75, in other embodiments, from about 1 to about 50, in other embodiments, from about 1 to about 25, and in other embodiments, from about 1 to about 10. In some embodiments, the polymer composition of the present invention will have a degree of polymerization (DP) of from about 5 to about 200, in other embodiments, from about 10 to about 200, in other embodiments, from about 20 to about 200, in other embodiments, from about 50 to about 200, in other embodiments, from about 100 to about 200, and in other embodiments, from about 150 to about 200. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

[0071] In one or more embodiments, the polymer composition of the present invention will have a number average molecular weight (M_n) of from about 0.5 kDa to about 100 kDa, preferably from about 0.5 kDa to about 50 kDa, and more preferably from about 0.5 kDa to about 5 kDa, as measured by size exclusion chromatography (SEC) or MALDI mass spectrometry or gel permeation chromatography (GPC). In some embodiments, the polymer composition of the present invention will have a number average molecular weight (M_n) of from about 1 kDa to about 100 kDa, in other embodiments, from about 1 kDa to about 75 kDa, in other embodiments, from about 1 kDa to about 50 kDa, in other embodiments, from about 1 kDa to about 25 kDa, in other embodiments, from about 1 kDa to about 15 kDa, in other embodiments, from about 10 kDa to about 100 kDa, in other embodiments, from about 40 kDa to about 100 kDa, and in other embodiments, from about 60 kDa to about 100 kDa as measured by size exclusion chromatography (SEC) or MALDI mass spectrometry or gel permeation chromatography (GPC). In some embodiments, the polymer composition of the present invention will have a number average molecular weight (M_n) of from about 0.5 kDa to about 10 kDa, as measured by size exclusion chromatography (SEC), MALDI mass spectrometry or gel permeation chromatography (GPC). Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

[0072] In one or more of these embodiments, the polymer composition of the present invention will have a mass distribution ($\mathcal{D}_m$) of from about 1 to about 2, preferably from about 1 to about 1.5, and more preferably from about 1 to about 1.2. In some embodiments, the polymer composition of the present invention will have a mass distribution ($\mathcal{D}_m$) of from about 1 to about 2, in other embodiments, from about 1.0 to about 1.8, in other embodiments, from about 1.0 to about 1.6, in other embodiments, from about 1.0 to about 1.4, in other embodiments, from about 1.0 to about 1.2, in other embodiments, from about 1.1 to about 2.0, in other embodiments, from about 1.3 to about 2.0, in other embodiments, from about 1.5 to about 2.0, in other embodiments, from about 1.7 to about 2.0, and in other embodiments, from about 1.9 to about 2.0.

Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

[0073] In one or more embodiments, the polymer composition of the present invention will have a zero sheer viscosity of from about 500 Pa·s to about 10,000 Pa·s, preferably from about 1,000 Pa·s to about 7,000 Pa·s, and more preferably from about 1,000 Pa·s to about 5,000 Pa·s, as measured by a rheometer. In some embodiments, the polymer composition of the present invention will have a zero sheer viscosity of from about 500 Pa·s to about 9,000 Pa·s, in other embodiments, from about 500 Pa·s to about 7,000 Pa·s, in other embodiments, from about 500 Pa·s to about 5,000 Pa·s, in other embodiments, from about 500 Pa·s to about 3,000 Pa·s, in other embodiments, from about 1000 Pa·s to about 10,000 Pa·s, in other embodiments, from about 3,000 Pa·s to about 10,000 Pa·s, in other embodiments, from about 6,000 Pa·s to about 10,000 Pa·s, and in other embodiments, from about 8,000 Pa·s to about 10,000 Pa·s, as measured by a rheometer.

[0074] In one or more embodiments, the polymer composition of the present invention in a 50% DEF solution by weight will have a zero sheer viscosity of from about 0.1 Pa·s to about 1.2 Pa·s, preferably from about 0.1 Pa·s to about 1.0 Pa·s, and more preferably from about 0.1 Pa·s to about 0.5 Pa·s, as measured by a rheometer. In some embodiments, the polymer composition of the present invention in a 50% DEF solution by weight will have a zero sheer viscosity of from about 0.2 Pa·s to about 1.2 Pa·s, in other embodiments, from about 0.4 Pa·s to about 1.2 Pa·s, in other embodiments, from about 0.6 Pa·s to about 2.0 Pa·s, in other embodiments, from about 0.8 Pa·s to about 2.0 Pa·s, in other embodiments, from about 1.0 Pa·s to about 2.0 Pa·s, in other embodiments, from about 0.1 Pa·s to about 1.1 Pa·s, in other embodiments, from about 0.1 Pa·s to about 0.9 Pa·s, in other embodiments, from about 0.1 Pa·s to about 0.7 Pa·s, in other embodiments, from about 0.1 Pa·s to about 0.5 Pa·s, and in other embodiments, from about 0.1 Pa·s to about 0.3 Pa·s, as measured by a rheometer. In one or more embodiments, the polymer composition of the present invention in a 70% polymer/30% DEF solution by weight will have a zero sheer viscosity of from about 1.5 Pa·s to about 2.5 Pa·s, preferably from about 1.8 Pa·s to about 2.4 Pa·s, and more preferably from

about 1.9 Pa·s to about 2.2 Pa·s, as measured by a rheometer. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

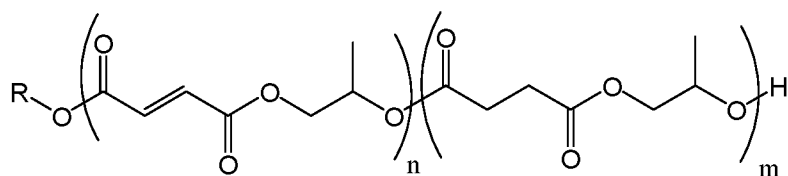
[0075] Further, and as set forth above, the addition of the succinic anhydride residues to the polymer composition of the present invention reduces their absorbance in the wavelengths used for 3D printing. As will be apparent to those of skill in the art, the absorbance is calculated based on the measured transmittance using the formula:

$$A = -\log(\%T/100\%) \quad (\text{Eq. 1})$$

where the transmittance (T) is the ratio of light that passes through the sample and absorbance (A) is the amount of light not transmitted (i.e. absorbed), relative to a reference standard. A high absorbance at the wavelength where the radical is generated by the photoinitiator reduces the number of available radicals for crosslinking, resulting in a polymer that does not crosslink or print well.

[0076] In various embodiments, the polymer composition of the present invention may have an absorbance at 3D printable wavelengths from about 305 nm to about 405 nm of from about 0.001 to about 0.3, preferably from about 0.001 to about 0.2, and more preferably from about 0.001 to about 0.1, as measured by a UV-Visible spectrometer. In some embodiments, the polymer composition of the present invention may have an absorbance at 3D printable wavelengths from about 305 nm to about 405 nm of from about 0.003 to about 0.3, in other embodiments, from about 0.05 to about 0.3, in other embodiments, from about 0.1 to about 0.3, in other embodiments, from about 0.15 to about 0.3, in other embodiments, from about 0.2 to about 0.3, in other embodiments, from about 0.001 to about 0.25, in other embodiments, from about 0.001 to about 0.2, in other embodiments, from about 0.001 to about 0.1, in other embodiments, from about 0.001 to about 0.01, as measured by a UV-Visible spectrometer. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

[0077] In one or more embodiments, the polymer composition of the present invention may have the formula:



where R is alkyl, alkene, alkyne or aromatic group; n is a mole fraction from about 0.50 to about 0.99 and m is a mole fraction from about 0.01 to about 0.50. In some embodiments, n may be a mole fraction from about 0.50 to about 0.95, in other embodiments, from about 0.50 to about 0.85, in other embodiments, from about 0.50 to about 0.75, in other embodiments, from about 0.50 to about 0.65, in other embodiments, from about 0.50 to about 0.55, in other embodiments, from about 0.60 to about 0.99, in other embodiments, from about 0.70 to about 0.99, in other embodiments, from about 0.80 to about 0.99, in other embodiments, from about 0.90 to about 0.99, and in other embodiments, from about 0.95 to about 0.99. In some embodiments, m may be a mole fraction from about 0.01 to about 0.50, in other embodiments, from about 0.01 to about 0.40, in other embodiments, from about 0.01 to about 0.30, in other embodiments, from about 0.01 to about 0.20, in other embodiments, from about 0.01 to about 0.10, in other embodiments, from about 0.01 to about 0.05, in other embodiments, from about 0.05 to about 0.50, in other embodiments, from about 0.10 to about 0.50, in other embodiments, from about 0.15 to about 0.50, in other embodiments, from about 0.25 to about 0.50, in other embodiments, from about 0.35 to about 0.50, and in other embodiments, from about 0.45 to about 0.50. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

In one or more embodiments, R may be or comprise a functional group selected from the group consisting of alkyne groups, propargyl groups, allyl groups, alkene groups, 4-dibenzocyclooctyne groups, cyclooctyne groups, ketone groups, aldehyde groups, tertiary halogen groups, and combinations thereof.

[0078] In a second aspect, the present invention is directed to a method of making the PPF-based 3D printable polymer composition described above by reacting maleic anhydride, succinic anhydride, propylene oxide and an initiating alcohol in the presence

of a magnesium or other organometallic catalyst to form a poly(propylene maleate-co-succinate) polymer intermediate having a maleic anhydride residue containing a *cis* double bond, and then isomerizing the *cis* double bond by reacting the poly(propylene maleate-co-succinate) polymer intermediate to form a poly(propylene fumarate-co-succinate) copolymer.

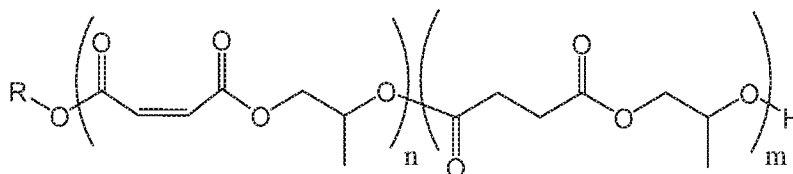
[0079] The initiating alcohol is not particularly limited provided that it has an available hydroxyl functional group and is capable of initiating ring opening copolymerization of a maleic anhydride monomer, a succinic anhydride monomer and a polypropylene oxide monomer, in the presence of a magnesium catalyst. Suitable initiating alcohols may include, without limitation, benzyl alcohol, propargyl alcohol, 4-hydroxybutan-2-one, 5-norbornen-2-ol, butanone, ethyl alcohol, isopropyl alcohol, tertiary butyl alcohol, or a combination thereof. In some embodiments, the initiating alcohol is a primary alcohol. In one more embodiments, the initiating alcohol may include a functional group to permit the addition of bioactive compounds or other useful moieties. Suitable functional groups may include, without limitation, alkyne groups, propargyl groups, allyl groups, alkene groups, 4-dibenzocyclooctyne groups, cyclooctyne groups, ketone groups, aldehyde groups, tertiary halogen groups, or a combination thereof. As used herein, the terms “bioactive molecule(s)” and “bioactive material(s)” are used interchangeably to refer to substances that influence cellular function and may include, without limitation, peptides, carbohydrates, proteins, oligonucleotides and small molecule drugs. The term “other useful moieties” refers to substances other than bioactive materials that provide an added benefit, such as fluorescent and other markers, small molecule dyes, and/or halide atoms. In some of these embodiments, the initiating alcohol may be, without limitation, propargyl alcohol, allyl alcohol, 4-dibenzocyclooctynol, 4-hydroxybutan-2-one, 3-hydroxypropan-2-one, 5-hydroxypentan-2-one, 6-hydroxyhexan-2-one, 7-hydroxyheptan-2-one, 8-hydroxyoctan-2-one, 5-norbornen-2-ol, α -bromoisobutyl 4-methanol benzyloxymethanoate, or a combination thereof. In various embodiments, the magnesium catalyst may be $\text{Mg}(\text{BHT})_2(\text{THF})_2$ or MgEt_2 , but is preferably $\text{Mg}(\text{BHT})_2(\text{THF})_2$.

[0080] In one or more of these embodiments, the maleic anhydride, succinic anhydride and propylene oxide are combined in a suitable sealed reaction vessel with an initiating alcohol, $\text{Mg}(\text{BHT})_2(\text{THF})_2$, and a suitable solvent. One of ordinary skill in the art will be able to select, configure or create a suitable reaction vessel without undue experimentation. In one or more of these embodiments, maleic anhydride and succinic anhydride are combined at a molar ratio of maleic anhydride to succinic anhydride of from about 100:1 to about 1:1, preferably from about 50:1 to about 1:1, and more preferably from about 2:1 to about 1:1. In some embodiments, the molar ratio of maleic anhydride to succinic anhydride from about 25:1 to about 1:1, in other embodiments, from about 10:1 to about 1:1, in other embodiments, from about 8:1 to about 1:1, in other embodiments, from about 6:1 to about 1:1, in other embodiments, from about 4:1 to about 1:1, and in other embodiments, from about 3:1 to about 1:1. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

[0081] As set forth above, the order in which the initiating alcohol, the maleic anhydride, succinic anhydride, propylene oxide and magnesium catalyst are combined has been found to affect color, and with it the absorbance, of the PPF-based 3D printable polymer composition of the present invention. (See FIG. 1) It has been found that bringing the catalyst into contact with either of the anhydride reagents (the maleic anhydride and succinic anhydride) prior to the addition of the initiating alcohol can result in adverse changes in the coordination chemistry of the catalyst, causing a darkening of the PPF-based 3D printable polymer produced thereby. Accordingly, in these embodiments, the alcohol is added to the reaction vessel first, followed by the catalyst, and then the other reagents. In some other embodiments, the catalyst is added to the reaction vessel first, followed by the alcohol, and then the other reagents. The order in which the propylene oxide is added, however, does not appear to have an effect on the absorbance of the polymer.

[0082] In these embodiments, the combination is heated until substantially all of the maleic anhydride, succinic anhydride and propylene oxide have reacted to form the poly(propylene maleate-co-succinate) copolymer intermediate. In one or more

embodiments, the poly(propylene maleate-co-succinate) copolymer intermediate may have the formula:



where R is alkyl, alkene, alkyne or aromatic group; n is a mole fraction from about 0.50 to about 0.99 and m is a mole fraction from about 0.01 to about 0.50. In various embodiments, n and m may be any of the mole fractions or range of mole fractions described above. As will be apparent, R will be or comprise the residue of the initiating alcohol. In some embodiments, R may be or comprise a functional group selected from the group consisting of alkyne groups, propargyl groups, allyl groups, alkene groups, 4-dibenzocyclooctyne groups, cyclooctyne groups, ketone groups, aldehyde groups, tertiary halogen groups, and combinations thereof.

[0083] Suitable solvents for this purpose are not particularly limited provided that the reaction proceeds and may include, without limitation, toluene, pentane, hexane, heptane, octane, THF, or a combination thereof. As will be apparent to those of skill in the art, the degree of polymerization may be controlled by controlling the available moles of initiator and/or the time and temperature of the polymerization reaction. In embodiments where the polymerization reaction is allowed to go to completion (where substantially all of the monomers have been reacted), the degree of polymerization may be controlled by controlling the available moles of initiating alcohol as a function of the total moles of available monomer. In some other embodiments, the degree of polymerization may be controlled by controlling ratio of the moles of initiating alcohol to either the moles of propylene oxide or the total moles of maleic anhydride and succinic anhydride used to form the copolymer.

[0084] In one or more of these embodiments, the sealed reaction vessel then is heated to a temperature of from about 40°C to about 80°C for from about 1 hours to about 48 hours (or until essentially all of the monomer is consumed) to produce a *cis* isomer poly(propylene maleate-co-succinate) intermediate of the poly(propylene

fumarate-co-succinate) copolymer composition of the present invention. In some embodiments, the sealed reaction vessel is heated to a temperature of from about 40°C to about 75°C, in other embodiments, from about 40°C to about 70°C, in other embodiments, from about 40°C to about 65°C, in other embodiments, from about 40°C to about 60°C, in other embodiments, from about 50°C to about 80°C, in other embodiments, from about 55°C to about 80°C, and in other embodiments, from about 60°C to about 80°C. In some embodiments, the sealed reaction vessel is heated for from about 1 hours to about 50 hours, in other embodiments, from about 1 hours to about 36 hours, in other embodiments, from about 1 hours to about 30 hours, in other embodiments, from about 1 hours to about 24 hours, in other embodiments, from about 6 hours to about 48 hours, in other embodiments, from about 12 hours to about 48 hours, and in other embodiments, from about 24 hours to about 48 hours. Here, as well as elsewhere in the specification and claims, individual range values can be combined to form additional non-disclosed ranges.

[0085] The poly(propylene maleate-co-succinate) copolymer intermediate may then be recovered by any suitable method known in the art for that purpose. In some embodiments, the poly(propylene maleate-co-succinate) copolymer intermediate may be recovered by precipitation into an excess of a non-solvent for the poly(propylene maleate-co-succinate) copolymer intermediate, such as diethyl ether, isopropyl alcohol, ethyl alcohol, hexane, or a combination thereof.

[0086] The recovered poly(propylene maleate-co-succinate) copolymer intermediate is then dried to remove remaining solvent. The poly(propylene maleate-co-succinate) copolymer intermediate may be dried using any suitable method known in the art including, but not limited to vacuum evaporation, air drying, rotary evaporation, or a combination thereof.

[0087] As set forth above, the *cis* double bonds in the maleic anhydride residues of the poly(propylene maleate-co-succinate) copolymer intermediate are next isomerized to arrive at the PPF based copolymer composition described above. As used herein, the terms “isomerize” and “isomerization” refer broadly to the conversion of the *cis*-isomer (PPM) to its *trans*-isomer (PPF) form or, in the context of a chemical reaction or process

(an “isomerization reaction”) to a reaction or process that converts the *cis*-isomer (PPM) to its *trans*-isomer (PPF) form. And as set forth above, the terms “isomerized residue of a maleic anhydride monomer,” “isomerized residues of maleic anhydride monomer,” “isomerized residue of a maleic anhydride” and “isomerized residues of maleic anhydride” specifically refers to one or more residues of the maleic anhydride monomer used to form the PPF-based 3D printable polymer composition of the present invention wherein the double bond has been isomerized from the *cis* (maleate) configuration to the *trans* (fumarate) configuration during formation of the poly(propylene fumarate-co-succinate) copolymer from the poly(propylene maleate-co-succinate) copolymer intermediate, as described below. While the isomerization of the poly(propylene maleate-co-succinate) copolymer intermediate does result in some other changes to the polymer, it should be understood that most general characteristics of the PPF-based 3D printable polymer composition of the present invention, such as the approximate M_n , D_m , and T_g ranges, are determined in the initial ROCOP reaction and do not change during the isomerization reaction.

[0088] In one or more of these embodiments, the poly(propylene maleate-co-succinate) copolymer intermediate is first dissolved in a suitable organic solvent. Suitable solvents for this purpose are not particularly limited provided that the reaction proceeds and may include, without limitation, chloroform, dichloromethane or a combination thereof. In one or more embodiments, the poly(propylene maleate-co-succinate) copolymer intermediate is dissolved in chloroform. Next, a quantity of an organic base, such as diethylamine, trimethylamine, or pyridine is added to the solution and it is heated to reflux temperature under an inert atmosphere to produce the poly(propylene fumarate-co-succinate) copolymer of the present invention.

[0089] In some of these embodiments, the solution is heated it to a reflux temperature under an inert atmosphere for from about 1 to about 48 hours (or until substantially all of poly(propylene maleate-co-succinate) copolymer intermediate has isomerized) to produce the poly(propylene fumarate-co-succinate) copolymer of the present invention. In some embodiments, the solution is refluxed for from about 1 hours to about 36 hours, in other embodiments, from about 1 hours to about 30 hours, in other

embodiments, from about 1 hours to about 24 hours, in other embodiments, from about 6 hours to about 48 hours, in other embodiments, from about 12 hours to about 48 hours, in other embodiments, from about 18 hours to about 48 hours, in other embodiments, from about 24 hours to about 48 hours, and in other embodiments, from about 36 hours to about 48 hours to produce the poly(propylene fumarate-co-succinate) copolymer of the present invention.

[0090] Finally, the poly(propylene fumarate-co-succinate) copolymer composition of the present invention may be washed with a buffer solution, such as a phosphate buffer solution, to remove residual monomer and amine and then dried to recover the poly(propylene fumarate-co-succinate) copolymer of the present invention. In one or more embodiments, the poly(propylene fumarate-co-succinate) copolymer composition of the present invention may be washed with a phosphate buffer solution and then dried by vacuum evaporation. The poly(propylene fumarate-co-succinate) copolymer may be purified by any suitable method known in the art for that purpose. In some of these embodiments, the poly(propylene fumarate-co-succinate) copolymer is purified by repeated washing in an excess of phosphate buffer saline solution or a suitable acid solution, combining the organic layers, and drying the resulting polymer *in vacuo* to produce the purified polymer.

EXPERIMENTAL

[0091] In order to evaluate and further reduce them to practice, the poly(propylene fumarate-co-succinate) copolymers of the present invention were synthesized and characterized as follows.

Materials

[0092] All materials were purchased from Millipore-Sigma and used as received unless noted below. $\text{Mg}(\text{BHT})_2(\text{THF})_2$ was synthesized using a modified preparation. (See, e.g., WO 2018/142384 and WO 2018/144849, and the disclosures of which are incorporated herein by reference in their entirety.) All solvents were purchased from Fisher and dried using an Pure Solv MD-3 solvent purification system (Innovative Technology Inc.) and degassed prior to use. Benzyl alcohol and propargyl alcohol were

distilled over calcium hydride and degassed. Maleic anhydride was sublimated and dried *in vacuo* over P₂O₅ for one week. Succinic anhydride was dried *in vacuo* over P₂O₅ for one week.

Instrumental Methods

[0093] Proton ¹H nuclear magnetic resonance (NMR) spectra were recorded using a Varian Mercury 300 spectrometer. Carbon ¹³C NMR spectra were recorded using a Varian NMRS 500 spectrometer. All chemical shifts were recorded in parts per million (ppm) relative to the reference peak of chloroform solvent at $\delta = 7.26$ and 77.16 ppm for ¹H and ¹³C spectra, respectively. Molecular masses were determined through size exclusion chromatography (SEC) using a Tosho EcoSec HLC-8320 GPC on TSKgel SuperMultiporeHZ-M columns in series with refractive index (RI) detector. Molecular masses were calculated using a calibration curve determined from poly(styrene) standards with tetrahydrofuran (THF) as the eluent flowing at 1.0 mL min⁻¹ and a sample concentration of 10.0 mg mL⁻¹.

[0094] MALDI-ToF mass spectra were recorded on a Bruker Ultra-Flex III MALDI-ToF/ToF mass spectrometer equipped with a Nd:YAG laser emitting at 355 nm. The instrument was operated in positive ion mode. All samples were dissolved in THF at a final concentration of 10 mg mL⁻¹. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) (20 mg mL⁻¹) served as a matrix and sodium trifluoroacetate (NaTFA) (10 mg mL⁻¹) as cationizing agent were prepared and mixed in the ratio 10:1. Matrix and sample solutions were applied onto the MALDI-ToF target plate by the sandwich method. FlexAnalysis software was used to analyze MALDI-ToF data.

General synthesis of *cis*-copolymer [poly(propylene maleate-*co*-propylene succinate)].

[0095] In a glovebox, 2.524 g (25.7 mmol) of maleic anhydride, 0.286 g (2.86 mmol) of succinic anhydride, 2.00 mL (28.6 mmol) of propylene oxide, 330 μ L (2.86 mmol) of propargyl alcohol as a initiator, 0.175 g (0.286 mmol) of Mg(BHT)₂(THF)₂ as a catalyst and 8.2 mL of toluene were placed in a Schlenk tube. The Schlenk tube was sealed with a PTFE plug and removed from the glovebox and heated to 80 °C in a

preheated aluminum block for 24 h. After the designated reaction time, the mixture was quenched with 4 mL of chloroform and precipitated with excess amount of diethyl ether. The copolymer (3.60 g; 80.5 %) was recovered after vacuum drying. ^1H NMR (300 MHz, 298 K, CDCl_3): δ = 6.40-6.16 (m, 25.7H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.34-5.05 (m, 12.5H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.74 (m, 2H, CCH_2O), 4.37-3.89 (m, 27.8H, $\text{OCH}_2\text{CHCH}_3$), 2.77-2.54 (m, 3.5H, $\text{OCH}_2\text{CHCH}_3$), 2.54-2.49 (m, 0.8H, CHC), 1.40-1.08 (m, 42.9, CHCH_3) ppm.

General isomerization procedure of *cis*-copolymer to trans-copolymer [poly(propylene fumarate-co-propylene succinate)].

[0096] To the solution of 3.00 g of poly(propylene maleate-co-propylene succinate) that were dissolved in 20 mL of chloroform, 300 μL (2.9 mmol) of diethyl amine was added and refluxed for 18 h under nitrogen atmosphere. The organic layer was washed with a 1M aqueous potassium phosphate solution (pH 6) and the polymer was recovered by vacuum drying. ^1H NMR (300 MHz, 298 K, CDCl_3): δ = 6.97-6.78 (m, 19.6H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.39-5.05 (m, 11.6H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.82 (d, 2.0H, CCH_2O), 4.45-4.00 (m, 24.8H, $\text{OCH}_2\text{CHCH}_3$), 2.58-2.49 (s, 1.2H, CHC), 1.40-1.03 (m, 40.0, CHCH_3) ppm.

3D printing fabrication.

[0097] The specimens for tensile testing were fabricated using an EnvisionTEC (Dearborn, MI) Perfactory 3 printer ($\lambda=405$ nm). The design files were created using SolidWorks software (Dassault Systems SolidWorks Corp., Waltham, MA). For tensile measurements, ASTM D360 type V tensile bars were printed with half sized x, y, z dimensions. The 3D printing resins were produced according to previously reported formula of photo initiators and light scattering agents (4.1 wt. %) with modification in the mixing ratio of copolymer and DEF. (See, Luo, Y.; Dolder, C. K.; Walker, J. M.; Mishra, R.; Dean, D.; Becker, M. L. Synthesis and Biological Evaluation of Well-Defined Poly(Propylene Fumarate) Oligomers and Their Use in 3D Printed Scaffolds. *Biomacromolecules* **2016**, 17 (2), 690–697, the disclosure of which is incorporated herein by reference in its entirety.) After 3D printing, the tensile bars were briefly washed sequentially with isopropyl alcohol, a mixture of 50 wt.% acetone and deionized

water and acetone, dried in air for 30 minutes and then post-cured for one hour in UV oven ($\lambda = 390 - 420$ nm).

[0098] The viscosity of the resin formulations was measured at 50-70 wt% polymer in diethyl fumarate (DEF) solution using an AERS-G2 rheometer. The premixed resin was placed on parallel plates (25 mm diameter) using a 1mm gap and data was collected via a frequency sweep ranging from 0.05 rad s^{-1} to 100 rad s^{-1} at 10 % strain while maintaining temperature at 25°C . Due to the fluctuation of data in low frequency, data from 3.15 rad s^{-1} to 100 rad s^{-1} was collected and the intercept of the regression curve was chosen as a representative viscosity of the resin formulation.

[0099] The mechanical properties measurements were conducted using Instron 5567 Series Universal Testing System. The force was measured with 10 kN load cell at 5 mm min^{-1} crosshead speed at room temperature. The elastic modulus was determined from the slope of the initial linear region. The values reported were obtained from the average of three measurements.

[00100] The swelling ratio of 3D printed product was measured using modified method of previous method. (See, Fisher, J. P.; Dean, D.; Mikos, A. G. Photocrosslinking Characteristics and Mechanical Properties of Diethyl Fumarate/Poly(Propylene Fumarate) Biomaterials. *Biomaterials* **2002**, 23 (22), 4333–4343, the disclosure of which is incorporated herein by reference in its entirety.) The tensile bars were placed into the 20 mL scintillation vial and immersed in 15 mL of toluene. After 48 hours, the samples were weighted (W_s) after wiping out the toluene on the surface. The weight of dried sample (W_d) is measured after 72 hours drying under vacuum. The swelling ration was calculated by the formula:

$$\text{Swelling ratio} = \frac{W_s - W_d}{W_s} \quad (\text{Eq. 2})$$

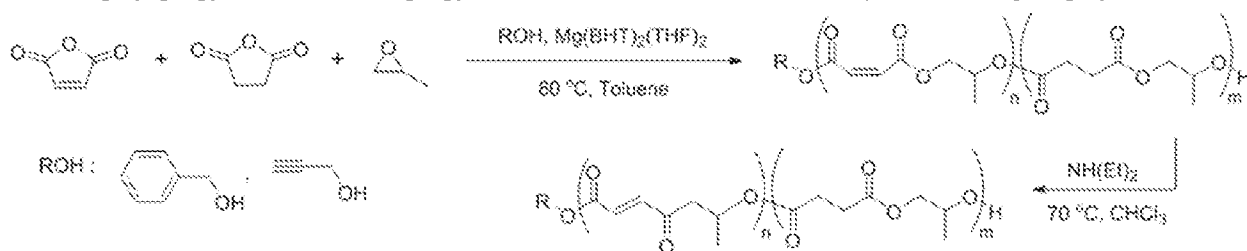
Results and Discussions

[00101] The ROCOP of maleic anhydride, succinic anhydride and propylene oxide was investigated at 7M concentration in toluene with $\text{Mg}(\text{BHT})_2(\text{THF})_2$ as a catalyst and benzyl alcohol or propargyl alcohol as a initiator at 80°C . After 24 hours, the reaction

mixture was precipitated into diethyl ether and the resulting *cis*-copolymer (poly(propylene maleate-*co*-propylene succinate)) (PPMPS) was isomerized using a catalytic amount of diethyl amine in chloroform (See, Scheme 1). The independent ROCOP of anhydrides and propylene oxide has been reported previously. However, this is the first attempt to use two different anhydrides in a one pot reaction. ^1H NMR spectroscopic analysis of PPMPS showed proton resonance peaks at $\delta = 6.27$ and 2.64 ppm, corresponding to *cis* alkene protons of the maleate unit and methylene protons of the succinate unit, respectively. Resonance peaks at $\delta = 4.78$ and 2.53 correspond to the methylene and alkyne protons on initiator propargyl alcohol, respectively (FIG. 2A). The preference of alternating copolymerization of anhydrides and propylene oxide was confirmed by the lack of significant numbers of proton resonances corresponding to the homopolymerization of propylene oxide ($\delta = 3.3$ -3.5), which were noted in previous studies. (See, e.g., Wilson, J. A.; Luong, D.; Kleinfehn, A. P.; Sallam, S.; Wesdemiotis, C.; Becker, M. L. Magnesium Catalyzed Polymerization of End Functionalized Poly(Propylene Maleate) and Poly(Propylene Fumarate) for 3D Printing of Bioactive Scaffolds. *J. Am. Chem. Soc.* **2018**, 140 (1), 277–284, the disclosure of which is incorporated herein by reference in its entirety.)

Scheme 1

Ring opening polymerization of maleic anhydride, succinic anhydride and propylene oxide to form poly(propylene maleate-*co*-propylene succinate) and isomerization of the resulting *cis*-polymer



[00102] Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-ToF MS) was performed to confirm the end-group and structure of polymer. The observed mass of 156 Da between two adjacent peaks revealed that the major repeat unit was propylene maleate. The magnification of one of these intensities showed that an addition of 2 Da from the initial monoisotopic mass to the next monoisotopic mass, which indicates a singular incorporation of succinate unit in the polymer chain (FIG. 3).

There were several distributions in the polymer chain that coincided with the expectation of an alternating copolymerization system, which are attributed to full polymeric repeating units or a half polymeric repeating units (i.e., one extra maleic anhydride or propylene oxide incorporated in the chain end). End group analysis showed that the polymer chains were initiated with alcohol initiator (FIG. 4). FIG. 5 is a MALDI-ToF MS plot of propargyl alcohol initiated poly(propylene maleate-co-propylene succinate) of DP 10 with 10 mol% succinate. These analysis results supported that the intended copolymer was synthesized successfully.

[00103] The monomer conversions were determined using ^1H NMR spectroscopy through integration of the monomeric anhydride resonances in crude reaction mixture. The conversions of maleic anhydride were higher than those of succinic anhydride, which were consistent with ^1H NMR spectroscopic analysis of the polymer after purification that showed lower succinate percentage compared with the maleate. The molecular masses of the polymers calculated based on ^1H NMR spectra were close to the targeted values regardless of the molar ratios of anhydrides, which demonstrates a high degree of control over the polymerization (Table 1).

Table 1
*Properties of poly(propylene maleate-co-propylene succinate) polymers
produced using $\text{Mg}(\text{BHT})_2(\text{THF})_2$ as a catalyst with
different alcohol initiators, target DPs and succinate content.^a*

Entry	[MAn]:[SAn]: [I]: [Cat.]	Initiator	MAn conv. (%) ^b	SAn conv. (%) ^b	Actual [MAn]:[SAn] ^c	M_n (kDa) ^c	M_n (kDa) ^d	$\bar{D}_M$ ^d
1	100:0:5:1	Benzyl alcohol	>99	-	100:0	4.0	2.9	1.40
2	95:5:5:1	Benzyl alcohol	98	63	97:3	3.9	2.6	1.36
3	90:10:5:1	Benzyl alcohol	>99	78	94:6	3.7	2.5	1.36
4	80:20:5:1	Benzyl alcohol	>99	71	89:11	3.7	2.4	1.36
5	70:30:5:1	Benzyl alcohol	95	91	77:23	3.7	2.6	1.42
6	50:50:5:1	Propargyl alcohol	99	98	58:42	3.5	2.4	1.77
7	0:100:5:1	Propargyl alcohol	-	97	0:100	4.5	1.9	1.39
8	90:10:10:1	Benzyl alcohol	>99	>99	94:6	2.3	1.6	1.35
9	80:20:10:1	Benzyl alcohol	>99	98	84:16	1.7	1.6	1.25
10	90:10:10:1	Propargyl alcohol	>99	97	94:6	2.0	1.6	1.37
11	80:20:10:1	Propargyl alcohol	>99	95	86:14	1.8	1.8	1.27

^a[Anhydride] = [PO] = 3.5 M in toluene, Temp_{rxn} = 80 °C, T_{rxn} = 24 h, Cat. = $\text{Mg}(\text{BHT})_2(\text{THF})_2$.

^bDetermined by ^1H NMR spectroscopy of crude reaction mixture. ^cDetermined by end-group analysis of ^1H NMR spectroscopy of final reaction product. ^dDetermined by SEC in THF against poly(styrene) standards.

[00104] To understand the structure of resulting copolymer further, a kinetic study of 4:1 ratio of maleic anhydride and succinic anhydride composition was conducted with a targeted degree of polymerization (DP) of 10. The conversion of anhydrides was *pseudo*-first order, indicating the controlled character of copolymerization. The slope of the first order monomer conversion versus time for maleic anhydride was higher than that of succinic anhydrides, demonstrating the incorporation of maleic anhydride into polymer chain was faster than that of succinic anhydride (FIG. 5A). Accordingly, the composition of maleate repeat units in the polymer chain was higher than the succinate composition (Table 2). These results suggested that the sequencing of the resulting copolymer was a gradient copolymer in nature rather than a random copolymer, wherein the polymer chain has higher maleate content at the beginning of the reaction and succinate content increased toward the end of the reaction. Molecular mass growth over monomer conversion was *pseudo*-linear with a maintained low $\bar{D}_M$ further enforcing the ability of for controlled copolymerization in line with previous studies (FIG. 5B).

Table 2
Kinetic study data of DP10, 20 % succinic anhydride reaction

		Time (h)				
Anhydride		3	6	12	18	24
Conversion (%)	MAn	33.9	62.8	79	95.6	97
	SAn	7.1	18.9	27.6	50	71.9
Mole fraction in copolymer (%)	MAn	95.0	94.4	92.4	90.7	89.2
	SAn	5.0	5.6	7.6	9.3	10.8

[00105] The diffusion ordered NMR spectroscopy (DOSY-NMR) shows one dominant distribution, indicating one polymer species as opposed to individual polymer chains from each anhydride polymerized (FIG. 2C). The ^{13}C NMR spectra showed that the resonance peaks corresponding to the carbonyl units of anhydrides are split to several peaks, rather than two peaks in the case of block or separated chain copolymers confirming that both anhydrides are incorporated in the polymer (FIG. 6).

[00106] The proton resonance peak at $\delta = 6.27$ ppm attributed to the *cis*-alkene proton environments of the maleate repeat units disappeared and a new proton resonance peak at $\delta = 6.85$ ppm corresponding to the *trans*-alkene proton environments of the fumarate units appeared, demonstrating complete isomerization of *cis*-copolymer to *trans*-copolymer (FIG. 2B). MALDI-ToF MS data showed that sequence and end group

fidelity of the copolymer are maintained after isomerization reaction (FIG. 7). Considering all data, maleic anhydride and succinic anhydride units are incorporated into one polymer species and the sequence of the polymer is a gradient copolymer composed of propylene fumarate repeat units and followed by propylene succinate repeat units with retained end-group fidelity.

[00107] In order to investigate the effect of copolymerization on the rheological properties of the copolymer, complex viscosity measurements were on the various poly(propylene fumarate) and poly(propylene fumarate-co-succinate) resin formulations (50 wt% DEF) at 25 °C. In previous studies, resin formulations containing 1000 to 2500 Da PPF in 50 wt% DEF solutions were used for photochemical 3D printing. (See, e.g., Luo, Y.; Dolder, C. K.; Walker, J. M.; Mishra, R.; Dean, D.; Becker, M. L. Synthesis and Biological Evaluation of Well-Defined Poly(Propylene Fumarate) Oligomers and Their Use in 3D Printed Scaffolds. *Biomacromolecules* **2016**, 17 (2), 690–697; Wilson, J. A.; Luong, D.; Kleinfehn, A. P.; Sallam, S.; Wesdemiotis, C.; Becker, M. L. Magnesium Catalyzed Polymerization of End Functionalized Poly(Propylene Maleate) and Poly(Propylene Fumarate) for 3D Printing of Bioactive Scaffolds. *J. Am. Chem. Soc.* **2018**, 140 (1), 277–284; and Walker, J. M.; Bodamer, E.; Krebs, O.; Luo, Y.; Kleinfehn, A.; Becker, M. L.; Dean, D. Effect of Chemical and Physical Properties on the In Vitro Degradation of 3D Printed High Resolution Poly(Propylene Fumarate) Scaffolds. *Biomacromolecules* **2017**, 18 (4), 1419–1425, the disclosures of which are incorporated herein by reference in their entirety.) Therefore resins containing DP 10 (1500 Da) and DP 20 (3000 Da) copolymers each possessing with succinate contents of 10 and 20 mole% were prepared in 50 wt% DEF solution. These resins were compared to formulations (50 wt% DEF) containing pure poly(propylene fumarate), DP 10 and DP 20, respectively. The frequency sweep data showed that the complex viscosity decreased with increasing succinate content in the poly(propylene fumarate-co-succinate) copolymer from 0 % to 20 %, in both DP 10 and DP 20 copolymer resins. The viscosity drop was more significant when succinate content was increased from 10 % to 20 % than compared to the difference in 0 % from 10 % succinate content (FIGS. 8A-B). The complex viscosity of the copolymer resins was measured with DP 10, 20% succinate

copolymer at increasing polymer concentrations. The viscosity was observed to increase as the polymer concentration in the resin formulation increased. While the viscosity limitation for photochemical 3D printing is highly dependent of the printer and print geometry, a survey of the literature values notes that the viscosity limitation in cDLP is around 2 Pa·s above which the print failures increase significantly. The viscosity of resin was determined to be 1.6 Pa·s at 70 wt% polymer in the resin, affording a 20 % increase in polymer content compared to resin containing pure DP 10 PPF. The viscosity of the resin was measured at elevated temperatures with 80 wt% and 100 wt% resin for 0% and 20% succinate copolymers. (See FIG. 9) The viscosity of succinate copolymer was lower than PPF and the viscosity decreased as the temperature increased. However, the reduction of viscosity was not significant enough to print the resin with DLP without elevating temperature more than 55 °C. This present a potential issue of changing the properties of the resin, such as viscosity and stability of photoinitiators, over the 3D printing process.

[00108] The 3D printing of a series of resin formulations (50, 60 and 70 wt% polymer) was performed to demonstrate that the resin could be 3D printed through cDLP into tensile bars according to ASTM D360 type V. The lengths of the x, y and z directions of the tensile bar were reduced to half because of the size limitation in the build plate of the 3D printer. The successful 3D printing of these resin formulations into tensile bars showed the retained 3D printability of the copolymers.

Table 3
*Tensile measurement result of 3D printed
tensile bars with different polymer content resins.*

Succinate content (%)	Polymer content (%)	E₀ (MPa)	UTS (MPa)	ε_{Break} (%)
0	50	224±8	15.9±1.5	8.6±1.4
10%	50	213±69	18.3±2.0	12.4±5.2
10%	60	177±25	15.6±1.1	14.6±0.1
10%	70	132±5	14.3±1.1	21.5±3.9
20%	50	188±6	13.4±1.8	15.6±4.5
20%	60	126±6	13.5±0.8	23.1±3.6
20%	70	98±6	12.2±0.5	27.5±2.6

[00109] To test the mechanical properties of 3D printed products, tensile modulus measurement were conducted after 1 hour post-curing in UV oven and compared with those of 3D printed tensile bars with 50 wt% of pure PPF polymer resin. In previous studies, (see, e.g., Fisher, J. P.; Dean, D.; Mikos, A. G. Photocrosslinking Characteristics and Mechanical Properties of Diethyl Fumarate/Poly(Propylene Fumarate) Biomaterials. *Biomaterials* **2002**, 23 (22), 4333–4343, the disclosure of which is incorporated herein by reference in its entirety) the elastic modulus (E_0) is in the range of 100 ~ 200 MPa, ultimate strength (UTS) is 10 ~ 13 MPa and ultimate strain is about 9 %. In this study, the elastic modulus of these tensile bars are 213 MPa and 188 MPa for 10 % succinate and 20 % succinate contents copolymer in 50 wt% polymer resin formula, respectively and its values are comparable to that of pure PPF (224 MPa). The elongation at break (ϵ_{Break}) for those bars are 12.4 ± 5.2 % and 15.6 ± 4.5 % for 10 % succinate and 20 % succinate contents copolymer in 50 wt% polymer resin formula, respectively, and are higher than that of pure PPF resin ($8.6 \% \pm 1.4$) (FIGS. 10A-B, Table 3). Comparing with previous data, E_0 and UTS are in similar range and ϵ_{Break} is higher value, indicates the promise of PPFS for bone tissue engineering application. In 10% succinate copolymer, E_0 are 213, 177 and 132, and ϵ_{Break} are 12.4, 14.6 and 21.5 for 50 wt%, 60 wt% and 70 wt% polymer contents in the resin, respectively. Similar trend is found for 20% succinate copolymer. This shows that as increasing the polymer contents in the resin, E_0 is decreasing and ϵ_{Break} is increasing while the UTS remains similar. These trends indicate that by changing the polymer content in the 3D printing resin, the elastic modulus and strain at break can be modulated (FIG. 10B).

[00110] To understand the origin of this trend, swelling test was conducted using the 3D printed tensile bar and the swelling ratio are calculated by modification of the previous study. (See, Fisher, J. P.; Dean, D.; Mikos, A. G. Photocrosslinking Characteristics and Mechanical Properties of Diethyl Fumarate/Poly(Propylene Fumarate) Biomaterials. *Biomaterials* **2002**, 23 (22), 4333–4343, the disclosure of which is incorporated herein by reference in its entirety.) The swelling ratio is related to the crosslinking density, so when crosslinking density is higher, then the swelling ratio is lower (FIG. 11). The swelling ratio of tensile bar are between 11 and 13 % which is

consistent regardless of the succinate contents in copolymer and the polymer contents in the resin formula, which means the crosslinking density is nearly consistent for all 3D printed tensile bars. This reveals that the mechanical property of the 3D printed product is mainly originated from the intrinsic properties of succinate unit rather than the crosslinking density difference. Comparing to the rigid double bond of fumarate unit, succinate has flexible saturated bond, therefore, as increasing succinate contents in the resin formula, the modulus is lower and the elongation at break is increasing.

Conclusions

[00111] It has been demonstrated herein that the ROCOP of propylene oxide, MAn and SAn using $\text{Mg}(\text{BHT})_2(\text{THF})_2$ yield copolymers with narrow molar mass distribution. A series of copolymers from renewable monomer feedstocks with various compositions, molecular mass and initiators were synthesized, isomerized and characterized. The MALDI-ToF MS, ^{13}C NMR analysis and kinetic studies revealed the resulting copolymers possess gradient sequencing. It has also been demonstrated that the incorporation of succinate units into poly(propylene fumarate) chains reduces the viscosity of copolymer. In turn, this reduction decreases the amount of DEF needed to 3D print the resin using stereolithographic methods, while the copolymer maintains photochemical printability. The mechanical properties of 3D printed product are modulated by the amount of succinate unit in the polymer and the contents of polymer in the resin formula. The retention of functionality of the initiating alcohol shows the possibility of post-functionalization of copolymer for additional bioactivity.

EXAMPLES

[00112] The following examples are offered to more fully illustrate the invention, but are not to be construed as limiting the scope thereof. Further, while some of examples may include conclusions about the way the invention may function, the inventor do not intend to be bound by those conclusions, but put them forth only as possible explanations. Moreover, unless noted by use of past tense, presentation of an example does not imply that an experiment or procedure was, or was not, conducted, or that

results were, or were not actually obtained. Efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperature), but some experimental errors and deviations may be present. Unless indicated otherwise, parts are parts by weight, molecular weight is weight average molecular weight, temperature is in degrees Centigrade, and pressure is at or near atmospheric.

Materials

[00113] All materials were purchased from Millipore-Sigma. The $\text{Mg}(\text{BHT})_2(\text{THF})_2$ was synthesized as using a modification of a previous reported method. (See, Wilson, J. A.; Hopkins, S. A.; Wright, P. M.; Dove, A. P., *Polym. Chem.*, 2014, 5, 2691-2694, the disclosure of which is incorporated herein by reference in its entirety.) All solvent were purchased from Fisher and dried using a Pure Solv MD-3 solvent purification system (Innovative Technology Inc.) and degassed prior to use. Benzyl alcohol and propargyl alcohol were distilled over calcium hydride and degassed. Maleic anhydride was sublimated and dried *in vacuo* over P_2O_5 for one week. Succinic anhydride was dried *in vacuo* over P_2O_5 for one week. All other materials were used as received.

Instrumental Methods

[00114] Proton (^1H) NMR spectra were recorded using a Varian Mercury 300 spectrometer. All chemical shifts were recorded in parts per million (ppm) relative to the reference peak of chloroform solvent at $\delta = 7.26$. Molecular masses were determined through size exclusion chromatography (SEC) using a Tosho EcoSec HLC-8320 GPC on TSKgel GMHHR-M columns in series with refractive index (RI) detector. Molecular masses were calculated using a calibration curve determined from poly(styrene) standards with tetrahydrofuran (THF) as the eluent flowing at 1.0 mL min^{-1} and a sample concentration of 10.0 mg mL^{-1} . MALDI-ToF mass spectra were recorded on a Bruker Ultra-Flex III MALDI-ToF/ToF mass spectrometer equipped with a Nd:YAG laser emitting at 355 nm. The instrument was operated in positive ion mode. All samples were dissolved in THF at a final concentration of 10 mg/mL . Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) (20 mg mL^{-1}) served as a matrix and

sodium trifluoroacetate (NaTFA) (10 mg mL⁻¹) as cationizing agent were prepared and mixed in the ratio 10 : 1. Matrix and sample solutions were applied onto the MALDI-ToF target plate by the sandwich method. FlexAnalysis software was used to analyze MALDI-ToF data. Complex viscosity data were obtained using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode. Complex viscosities are measured at room temperature at 10% strain in 0.5 to 100 rad/s angular frequency range. Zero sheer viscosity is calculated by intercept of regression curve using the data ranging from 3 to 100 rad/s. UV-Vis data were collected using a BioTek Synergy Mx microplate reader (UV visible spectrometer) at 1% concentration in THF solution.

General synthesis of PPM copolymer

[00115] In a glovebox, 28.6 mmol of maleic anhydride, 28.6 mmol of propylene oxide, dedicated amount of alcohol (ranging from 2.86 to 1.43 mmol) as a initiator, 0.286 mmol of Mg(BHT)₂(THF)₂ as a catalyst and 8.2 mL of toluene were placed in the vacuum Schlenk tube. The Schlenk tube was sealed with PTFE plug and removed from the glovebox and heated to 80 °C in the preheated heating block for 24 hours. After designed reaction time, the mixture was precipitated with excess amount of diethyl ether and the precipitated solid was dried under vacuum.

Comparative Example 1

Polymerization for DP 10 poly(propylene maleate) (PPM)

[00116] In a glove box, maleic anhydride (2.80 g, 28.5 mmol), propylene oxide (2.00 mL, 28.5 mmol), propargyl alcohol (164.8 uL, 2.85 mmol), Mg(BHT)₂(THF)₂ (348 mg, 0.573 mmol), and 8.2 mL of toluene were added to a Schlenk tube. The Schlenk tube was sealed with cap and heated to 80 °C for 24 hours. The resulting copolymer was precipitated into 200 mL of diethyl ether. After removing the solvent and drying under vacuum, 4.06 g (91.0 %) of PPM was recovered. The resulting copolymer was characterized by ¹H NMR ((300 MHz, 298 K, CDCl₃): 6.36-6.18 (m, 22.75H, C=OCHCHC=O), 5.35-5.14 (m, 11.4H, CH₂CHCH₃O), 4.82 (d, 2.0H, CCH₂O), 4.37-4.00 (m, 24.8H, OCH₂CHCH₃), 2.58-2.49 (s, 0.9H, CHC), 1.40-1.08 (m, 77.9, CHCH₃)) The ¹H NMR spectrum of the DP 10 PPM polymer is shown as FIG. 12. The degree of polymerization was confirmed by nuclear magnetic resonance imagery (NMR) and the

number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Comparative Example 2

Polymerization for DP 20 poly(propylene maleate) (PPM)

[00117] A DP 20 poly(propylene maleate) (PPM) was synthesized using the method set forth in Comparative Example 1, except 148.2 uL of benzyl alcohol was added (i.e., 2.80 g of maleic anhydride, 2 mL of propylene oxide, 148.6 uL of benzyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used) and 4.02 g (90.0 %) of PPM copolymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 7.36 (s, 5H, Ar), 6.36-6.18 (m, 47.5H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.35-5.14 (m, 26.4H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.37-4.00 (m, 49.4H, $\text{OCH}_2\text{CHCH}_3$), 1.40-1.08 (m, 75.9, CHCH_3)). The ^1H NMR spectrum of the DP 20 PPM copolymer is shown as FIG. 13. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 1

Copolymer Synthesis for DP 20 polymer with a 5 mol% succinic anhydride feed ratio

[00118] A DP 20 polymer with a 5 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 2.664 g of maleic anhydride and 143.2 mg of succinic anhydride were added instead of 2.80 g maleic anhydride (i.e., 2.664 g of maleic anhydride, 0.143 g of succinic anhydride, 2 mL of propylene oxide, 148.6 uL of benzyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$), 4.42 g (99.0 %) of copolymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 7.36 (s, 5.0H, Ar), 6.36-6.18 (m, 49.0H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.35-5.14 (m, 26.9H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.37-4.00 (m, 52.7H, $\text{OCH}_2\text{CHCH}_3$), 2.67-2.55 (m, 2.7H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 1.40-1.08 (m, 77.9, CHCH_3)). A ^1H NMR spectrum for the DP 20 copolymer with 5 mol% succinic anhydride is shown as FIG. 14. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer

were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 2

Polymerization for DP 20 and 10 mol% succinic anhydride feed ratio

[00119] A DP 20 copolymer with a 10 mol% succinic anhydride feed ratio was synthesized following the procedure shown in Comparative Example 1, except that 2.524 g of maleic anhydride and 286 mg of succinic anhydride were used instead of 2.80 g maleic anhydride (i.e., 2.524 g of maleic anhydride, 0.286 g of succinic anhydride, 2 mL of propylene oxide, 148.6 μ L of benzyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 4.46 g (99.8 %) of copolymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 7.36 (s, 5.0H, Ar), 6.36-6.18 (m, 43.0H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.35-5.14 (m, 25.0H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.37-4.00 (m, 48.2H, $\text{OCH}_2\text{CHCH}_3$), 2.67-2.55 (m, 5.8H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 1.40-1.08 (m, 72.0, CHCH_3)). A ^1H NMR spectrum for the DP 20, 10 mol% succinic anhydride copolymer is attached hereto as FIG. 15. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution (D_m) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 3

Polymerization for DP 20 and 20 mol% succinic anhydride feed ratio

[00120] A DP 20 polymer with a 20 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except 2.244 g of maleic anhydride and 572 mg of succinic anhydride were added instead of 2.80 g maleic anhydride (i.e., 2.244 g of maleic anhydride, 0.572 g of succinic anhydride, 2 mL of propylene oxide, 148.6 μ L of benzyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 4.41 g (98.6 %) of the copolymer were recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 7.36 (s, 5.0H, Ar), 6.36-6.18 (m, 41.4H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.35-5.14 (m, 25.0H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.37-4.00 (m, 48.9H, $\text{OCH}_2\text{CHCH}_3$), 2.67-2.55 (m, 10.0H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 1.40-1.08 (m, 72.1, CHCH_3)). A

¹H NMR spectrum of the DP 20, 20 mol% succinic anhydride feed copolymer is shown at FIG. 16. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 4

Polymerization for DP 20 and 30 mol% succinic anhydride feed ratio

[00121] A DP 20 polymer with a 30 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 1.964 g of maleic anhydride and 858 mg of succinic anhydride were added instead of 2.80 g maleic anhydride (i.e., 1.964 g of maleic anhydride, 0.858 g of succinic anhydride, 2 mL of propylene oxide, 148.6 μ L of benzyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 4.40 g (98.2 %) of copolymer was recovered. The resulting copolymer was characterized by ¹H NMR ((300 MHz, 298 K, CDCl_3): 7.36 (s, 5.0H, Ar), 6.36-6.18 (m, 34.2H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.35-5.14 (m, 24.5H, $\text{CH}_2\text{CHCH}_3\text{O}$, ArCH_2O), 4.37-4.00 (m, 47.1H, $\text{OCH}_2\text{CHCH}_3$), 2.67-2.55 (m, 20.5H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 1.40-1.08 (m, 71.9, CHCH_3). A ¹H NMR spectrum for the DP 20, 30 mol% succinic anhydride feed copolymer is shown in FIG. 17. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 5

Polymerization for DP 20 and 50 mol% succinic anhydride feed ratio

[00122] A DP 20 polymer with a 50 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 1.40 g of maleic anhydride and 1.43 g of succinic anhydride was added instead of 2.80 g maleic anhydride and 82.5 μ L of propargyl alcohol was added instead of benzyl alcohol (i.e., 1.40 g of maleic anhydride, 1.43 g of succinic anhydride, 2 mL of propylene oxide, 148.6 μ L of benzyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 4.15 g (92.4 %) of copolymer was recovered. The resulting copolymer was characterized by ¹H NMR ((300

MHz, 298 K, CDCl_3): 6.40-6.16 (m, 30.9H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.34-5.05 (m, 25.6H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.74 (m, 2H, CCH_2O), 4.37-3.89 (m, 56.6H, $\text{OCH}_2\text{CHCH}_3$), 2.77-2.54 (m, 44.9H, $\text{OCH}_2\text{CHCH}_3$), 2.54-2.49 (m, 1.3H, CHC), 1.40-1.08 (m, 77.9, CHCH_3). A ^1H NMR spectrum for the DP 20, 50 mol% succinic anhydride feed copolymer is shown in FIG. 18. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution (D_m) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 6

Polymerization for DP 20 and 100 mol% succinic anhydride feed ratio

[00123] A DP 20 polymer with a 100 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 2.86 g of succinic anhydride was added instead of 2.80 g maleic anhydride and 82.5 μL of propargyl alcohol was added instead of benzyl alcohol (i.e., 2.86 g of succinic anhydride, 2 mL of propylene oxide, 82.5 μL of propargyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 4.15 g (92.4 %) of copolymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.40-6.16 (m, 6.4H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.34-5.05 (m, 26.8H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.67 (m, 2H, CCH_2O), 4.37-3.89 (m, 59.1H, $\text{OCH}_2\text{CHCH}_3$), 2.77-2.49 (m, 109.2H, $\text{OCH}_2\text{CHCH}_3$, CHC), 1.40-1.08 (m, 90.7, CHCH_3). A ^1H NMR spectrum for the DP 20, 100 mol% succinic anhydride feed copolymer is shown in FIG. 19.

Example 7

Polymerization for DP 10 and 10 mol% succinic anhydride feed ratio

[00124] A DP 10 polymer with a 10 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 2.524 g of maleic anhydride and 286 mg of succinic anhydride were added instead of 2.80 g maleic anhydride and 165 μL of propargyl alcohol was added instead of benzyl alcohol (i.e., 2.524 g of maleic anhydride, 0.286 g of succinic anhydride, 2 mL of propylene oxide, 330 μL of propargyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 3.60 g (80.5 %) of copolymer was recovered. The resulting copolymer was characterized

by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.40-6.16 (m, 25.7H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.34-5.05 (m, 12.5H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.74 (m, 2H, CCH_2O), 4.37-3.89 (m, 27.8H, $\text{OCH}_2\text{CHCH}_3$), 2.77-2.54 (m, 3.5H, $\text{OCH}_2\text{CHCH}_3$), 2.54-2.49 (m, 0.8H, CHC), 1.40-1.08 (m, 42.9, CHCH_3). A ^1H NMR spectrum for the DP 10, 10 mol% succinic anhydride feed copolymer is shown at FIG. 20. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Example 8

Polymerization for DP 10 and 20 mol% succinic anhydride feed ratio

[00125] A DP 10 polymer with a 20 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 2.244 g of maleic anhydride and 572 mg of succinic anhydride were added instead of 2.80 g maleic anhydride and 165 μL of propargyl alcohol was added instead of benzyl alcohol (i.e., 2.244 g of maleic anhydride, 0.572 g of succinic anhydride, 2 mL of propylene oxide, 165 μL of propargyl alcohol, 174 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ were used). 4.35 g (97.2 %) of copolymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.40-6.16 (m, 22.3H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.34-5.05 (m, 11.9H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.74 (m, 2H, CCH_2O), 4.37-3.89 (m, 25.7H, $\text{OCH}_2\text{CHCH}_3$), 2.77-2.54 (m, 7.1H, $\text{OCH}_2\text{CHCH}_3$), 2.54-2.49 (m, 0.9H, CHC), 1.40-1.08 (m, 38.9, CHCH_3). A ^1H NMR spectrum for the DP 10, 20 mol% succinic anhydride feed copolymer is shown as FIG. 21. The degree of polymerization was confirmed by NMR and the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC). The results are reported on Table 4, below.

Table 4
Polymer analysis data for Examples 1-9 and Comparative Examples 1-2

Entry	Feed Ratio		Composition		Degree Polymerization		GPC	
	MAN	SAN	MAN	SAN	Expected	NMR	M _n (kDa)	Đ _M
C. Example 1	100	-	100	0	10	11	2.0	1.30
C. Example 2	100	-	100	0	20	24	2.9	1.29
Example 1	95	5	97	3	20	24	2.6	1.36
Example 2	90	10	94	6	20	23	2.5	1.36
Example 3	80	20	89	11	20	23	2.4	1.36
Example 4	70	30	77	23	20	23	2.6	1.42
Example 5	50	50	58	42	20	25	2.4	1.77
Example 6	0	100	0	100	20	28	1.9	1.39
Example 7	90	10	94	6	10	13	1.6	1.37
Example 8	80	20	86	14	10	12	1.8	1.27

General procedure for isomerization of copolymer

[00126] To the solution of 3 g of copolymer that were dissolved in 20 mL of chloroform, 300 uL of diethyl amine was added and refluxed for 18 hours under nitrogen atmosphere. The organic layer was washed with 1M sodium phosphate aqueous solution and the polymer was recovered by evaporation under vacuum.

Comparative Example 3

PPF synthesis (Isomerization of the Polymer of Comparative Example 1)

[00127] 3 g of the polymer that was recovered from Comparative Example 1 was dissolved in 20 mL of chloroform and 0.30 mL of diethylamine was added to the solution. The solution was heated to reflux under nitrogen flow for 12 hours. The organic solution was then washed with phosphate buffer solution and the isomerized polymer was recovered by vacuum evaporation. The resulting copolymer was characterized by ¹H NMR ((300 MHz, 298 K, CDCl₃): 6.97-6.78 (m, 19.6H, C=OCHCHC=O), 5.39-5.05 (m, 11.6H, CH₂CHCH₃O), 4.82 (d, 2.0H, CCH₂O), 4.45-4.00 (m, 24.8H, OCH₂CHCH₃), 2.58-2.49 (s, 1.2H, CHC), 1.40-1.03 (m, 40.0, CHCH₃). A ¹H NMR spectrum of DP 10 poly(propylene fumarate) (PPF) is attached hereto as FIG. 22. The degree of polymerization was confirmed by NMR, the number average molecular weight (M_n) and mass distribution (Đ_m) for the copolymer were measured by gel permeation

chromatography (GPC), the complex viscosity of polymer in 50% DEF solution (by weight) was measured using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode at room temperature at 10% strain in 0.5 to 100 rad/s angular frequency range and the zero shear viscosity was calculated by finding the y intercept of a regression curve of frequency sweep data in the range from 3 rad/s to 100 rad/s, as set forth above. The results are reported on Table 5, below.

Comparative Example 4

PPF synthesis (Isomerization of the Polymer of Comparative Example 2)

[00128] A DP 20 PPF polymer was synthesized following same procedure shown in Comparative Example 3, except that the polymer that was recovered from Comparative Example 2 was used (rather than the polymer recovered from Comparative Example 1) and the isomerized polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 7.36 (s, 5H, Ar), 7.02-6.78 (m, 39.4H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.37-5.07 (m, 25.1H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.47-4.00 (m, 47.0H, $\text{OCH}_2\text{CHCH}_3$), 1.40-0.98 (m, 74.5, CHCH_3). A ^1H NMR spectrum of DP 20 poly(propylene fumarate) (PPF) polymer is shown in FIG. 23. The degree of polymerization was confirmed by NMR, the number average molecular weight (M_n) and mass distribution (D_m) for the copolymer were measured by gel permeation chromatography (GPC), and the complex viscosity of polymer in 50% DEF solution (by weight) was measured using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode at room temperature at 10% strain in 0.5 to 100 rad/s angular frequency range and the zero shear viscosity was calculated by finding the y intercept of a regression curve of frequency sweep data in the range from 3 rad/s to 100 rad/s, as set forth above. The results are reported on Table 5.

Example 9

10%, DP=10 Copolymer Isomerization

[00129] The polymer that was recovered from Example 7 was isomerized following procedures used in Comparative Example 3, above, and the isomerized polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 22.1H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 13.2H, $\text{CH}_2\text{CHCH}_3\text{O}$),

4.80-4.74 (m, 2H, CCH_2O), 4.40-3.98 (m, 29.7H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 5.7H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.0H, CHC), 1.40-0.98 (m, 48.8, CHCH_3). A ^1H NMR spectrum of DP 10 with a 10 mol% succinic anhydride feed ratio copolymer after isomerization is shown in FIG. 24. In addition, the degree of polymerization was confirmed by NMR, the number average molecular weight (M_n) and mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC), and the complex viscosity of polymer in 50% DEF solution (by weight) was measured using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode at room temperature at 10% strain in 0.5 to 100 rad/s angular frequency range and the zero shear viscosity was calculated by finding the y intercept of a regression curve of frequency sweep data in the range from 3 rad/s to 100 rad/s, as set forth above. The results are reported on Table 5, below.

Example 10

20%, DP=10 Copolymer Isomerization

[00130] The polymer that was recovered from Example 8 was isomerized following procedures used in Comparative Example 3, above, and the isomerized polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 19.7H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 12.7H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.74 (m, 2H, CCH_2O), 4.40-3.98 (m, 27.9H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 9.7H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.1H, CHC), 1.40-0.98 (m, 43.1, CHCH_3). A ^1H NMR spectrum of the DP 10 with a 20 mol% succinic anhydride feed ratio copolymer after isomerization is shown in FIG. 25. The molecular mass of the polymer was further characterized by size exclusion chromatography (SEC). A SEC chromatograph for the DP10 copolymer with a 20% succinic anhydride feed rate is shown in FIG. 26. In addition, the degree of polymerization was confirmed by NMR, the number average molecular weight (M_n) and molecular mass distribution ($\mathcal{D}_m$) for the copolymer were measured by gel permeation chromatography (GPC), and the complex viscosity of polymer in 50% DEF solution was measured using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode at room temperature at 10%

strain in 0.5 to 100 rad/s angular frequency range and the zero sheer viscosity was calculated by finding the y intercept of a regression curve of frequency sweep data in the range from 3 rad/s to 100 rad/s, as set forth above. The results are reported on Table 5, below.

Example 11

10%, DP=20 Copolymer Isomerization

[00131] The polymer that was recovered from Example 2 was isomerized following procedures used in Comparative Example 3, above, and the isomerized polymer was recovered. The resulting copolymer was characterized by ^1H NMR (300 MHz, 298 K, CDCl_3): 7.37 (s, 5.0H, Ar), 6.99-6.80 (m, 35.4H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.39-5.10 (m, 24.8H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.43-4.00 (m, 46.5H, $\text{OCH}_2\text{CHCH}_3$), 2.72-2.54 (m, 7.7H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 1.40-1.08 (m, 73.2, CHCH_3). A ^1H NMR spectrum of the DP 20 copolymer with 10 mol% succinic anhydride feed ration after isomerization is shown in FIG. 27. In addition, the degree of polymerization was confirmed by NMR, the number average molecular weight (M_n) and mass distribution (D_m) for the copolymer were measured by gel permeation chromatography (GPC), and the complex viscosity of polymer in 50% DEF solution (by weight) was measured using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode at room temperature at 10% strain in 0.5 to 100 rad/s angular frequency range and the zero sheer viscosity was calculated by finding the y intercept of a regression curve of frequency sweep data in the range from 3 rad/s to 100 rad/s, as set forth above. The results are reported on Table 5, below.

Example 12

20%, DP 20 Copolymer Isomerization

[00132] The polymer that was recovered from Example 3 was isomerized following procedures used in Comparative Example 3, above, and the isomerized polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 7.37 (s, 5.0H, Ar), 6.99-6.80 (m, 32.4H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.39-5.10 (m, 21.6H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.43-4.00 (m, 40.7H, $\text{OCH}_2\text{CHCH}_3$), 2.72-2.54 (m, 11.2H,

C=OCH₂CH₂C=O), 1.40-1.08 (m, 65.7, CHCH₃). A ¹H NMR spectrum of DP 20 and 20 mol% succinic anhydride feed copolymer after isomerization is shown as FIG. 28. The degree of polymerization was confirmed by NMR, the number average molecular weight (M_n) and mass distribution (Đ_m) for the copolymer were measured by gel permeation chromatography (GPC), and the complex viscosity of polymer in 50% DEF solution (by weight) was measured using TA instrument ARES-R2 rheometer with 25 mm diameter plate under frequency sweep mode at room temperature at 10% strain in 0.5 to 100 rad/s angular frequency range and the zero sheer viscosity was calculated by finding the y intercept of a regression curve of frequency sweep data in the range from 3 rad/s to 100 rad/s, as set forth above. The results are reported on Table 5, below.

Table 5.
*Polymer analysis data (after isomerization) for
Examples 9-12 and Comparative Examples 3-4*

Entry	Composition		Degree Polymerization		GPC		Zero Sheer Viscosity* (Pa·s)
	Fm	SAn	Expected	NMR	M _n (kDa)	Đ _M	
C. Example 3	100	0	10	10	2.2	1.30	0.703
C. Example 4	100	0	20	20	3.2	1.30	1.166
Example 9	89	11	10	13	1.8	1.37	0.445
Example 10	81	19	10	13	1.6	1.28	0.101
Example 11	90	10	20	23	2.6	1.37	0.912
Example 12	85	15	20	20	2.0	1.34	0.500

*for the copolymer in a 50% DEF solution.

Example 13

Complex Viscosity of the PPF Copolymer of Comparative Examples 3 and 4 and Examples 9 -12

[00133] 1 g of the trans polymers produced in Comparative Examples 3 and 4 and Examples 9-12, were mixed with 1 g DEF and heated to 45 °C for 5 hours to make homogenous solution. After cooled down to the room temperature, complex viscosities of the solution were measured under frequency sweep mode from 0.5 rad/s to 100 rad/s angular frequency with 10 % strain using TA instrument ARES-R2 rheometer with 25 mm diameter plate. Zero sheer viscosities were calculated by the intercept of regression curve of the complex viscosity data frequency range of from 3.0 rad/s to 100 rad/s, to exclude highly fluctuated data (unstable data).

[00134] The frequency sweep data for isomerized copolymers solutions with a DP of 10 or 20 and having 0, 10, or 20 mole% succinate units is shown Table 6, below and in FIG. 29. As can be seen, as the content of succinate units in copolymer increases, the viscosity of copolymer/DEF solution is reduced. Copolymer solutions having a DP or 10 with a 20% succinate content have viscosities as low as 0.1 Pa·s.

Table 6
Complex Viscosity Results for Examples 9-12 and Comparative Examples 3-4

Angular Frequency (rad/s)	Complex Viscosity (Pa·s)					
	DP10 PPF (C.Ex 3)	DP10 10% (Ex 9)	DP10 20% (Ex 10)	DP20 PPF (C.Ex 4)	DP20 10% (Ex 11)	DP20 20% (Ex 12)
0.5	0.703901	0.467579	0.0772745	1.17296	0.968098	0.544875
0.629463	0.683699	0.366862	0.131156	1.18433	0.958519	0.567061
0.792447	0.756152	0.468469	0.0980775	1.15025	0.984082	0.550402
0.997631	0.734811	0.447065	0.115936	1.18324	0.952094	0.546718
1.25594	0.717132	0.473277	0.0989156	1.16399	0.96089	0.538342
1.58114	0.714829	0.43669	0.107443	1.17956	0.952207	0.555992
1.99054	0.7248	0.447248	0.11673	1.16621	0.936917	0.536908
2.50594	0.725384	0.467103	0.0975662	1.16552	0.937252	0.525661
3.15479	0.714643	0.450362	0.105024	1.1632	0.925644	0.507559
3.97164	0.706825	0.458056	0.0970946	1.16868	0.919568	0.50513
5	0.697849	0.438931	0.0945988	1.16297	0.919298	0.519987
6.29463	0.704538	0.445664	0.103416	1.16756	0.913645	0.502308
7.92447	0.702124	0.443487	0.0992335	1.16642	0.909694	0.495175
9.97631	0.69881	0.441341	0.101272	1.16545	0.908079	0.494514
12.5594	0.697505	0.440583	0.100379	1.1652	0.902638	0.490539
15.8114	0.696101	0.441241	0.0984171	1.16565	0.902231	0.486219
19.9054	0.693042	0.440765	0.101762	1.16407	0.899728	0.482542
25.0594	0.69375	0.437903	0.0996049	1.16583	0.900363	0.480237
31.5479	0.691366	0.43901	0.100344	1.16609	0.898091	0.478922
39.7164	0.688902	0.438549	0.101141	1.16455	0.897666	0.476336
50	0.689307	0.44039	0.100247	1.16397	0.894767	0.473495
62.9463	0.686441	0.43679	0.0994956	1.1643	0.893999	0.472632
79.2447	0.68495	0.436568	0.0987093	1.16092	0.890857	0.469378
100	0.685156	0.440266	0.0930185	1.16047	0.900608	0.473655

Example 14*24%, DP 6 Poly(propylene fumarate-co-succinate) Copolymer Synthesis*

[00135] A DP 6 polymer with a 20 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 112 g of maleic anhydride, 29 g of succinic anhydride, 100 mL of propylene oxide and 16.6 mL of propargyl alcohol were added. 8.7 g of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ and 410 mL of toluene were used and 160 g of polymer was collected. 140 g of obtained polymer was isomerized following procedures used in Comparative Example 3, above, and the trans polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 9.0H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 6.1H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.54 (m, 2H, CCH_2O), 4.40-3.98 (m, 13.7H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 5.4H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.1H, CHC), 1.40-0.98 (m, 21.3, CHCH_3). The DP that calculated by NMR is 6 and succinate content is 24%.

Example 15*16%, DP 10 Poly(propylene fumarate-co-succinate) Copolymer Synthesis*

[00136] A DP 10 polymer with a 20 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 112 g of maleic anhydride, 29 g of succinic anhydride, 100 mL of propylene oxide and 8.3 mL of propargyl alcohol were added. 8.7 g of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ and 410 mL of toluene were used and 150 g of polymer was collected. 130 g of obtained polymer was isomerized following procedures used in Comparative Example 3, above, and the trans polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 15.2H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 10.2H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.54 (m, 2H, CCH_2O), 4.40-3.98 (m, 23.2H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 5.9H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.0H, CHC), 1.40-0.98 (m, 36.2, CHCH_3). The DP that calculated by NMR is 10 and succinate content is 16%.

Example 16*26%, DP 10 Poly(propylene fumarate-co-succinate) Copolymer Synthesis*

[00137] A DP 10 polymer with a 20 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 112 g of maleic anhydride, 29 g of succinic anhydride, 100 mL of propylene oxide and 8.3 mL of propargyl alcohol were added. 8.7 g of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ and 410 mL of toluene were used and 230 g of polymer was collected. 220 g of obtained polymer was isomerized following procedures used in Comparative Example 3, above, and the trans polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 14.7H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 10.8H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.54 (m, 2H, CCH_2O), 4.40-3.98 (m, 26.8H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 10.5H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.1H, CHC), 1.40-0.98 (m, 40.7, CHCH_3). The DP that calculated by NMR is 11 and succinate content is 26%.

Example 17*Complex Viscosity of the Poly(propylene fumarate-co-succinate) Copolymers*

[00138] Solutions containing the PPF (trans) copolymers of Examples 14, 15, 16 with DEF were prepared by dissolving the trans copolymers of Example 14, 15, and 16 in DEF at 45 °C at different weight ratio of polymer to DEF. The complex viscosities trans copolymer/DEF solutions having polymer contents of 50%, 70%, 80% and 90% by weight were measured by rheometer as set forth above and their zero shear viscosities were calculated from those complex viscosities following the procedures set forth in Example 13. The results are shown on Table 7, below.

Table 7
Zero Shear Viscosity Results for Examples 9-12 and Comparative Examples 3-4

Entry	DP	Composition		Zero sheer viscosity (Pa·s)				
		Fm	SAn	50 % polymer*	70 % Polymer*	80 % Polymer*	90 % polymer*	100 % polymer*
Example 14	6	76	24	0.12	1.59	9.61	43.27	1090
Example 15	10	84	16	0.16	2.29	14.32	106.31	3510
Example 16	11	74	26	0.18	2.36	13.73	85.75	5670

*Weight percent polymer in DEF solution

[00139] As can be seen, the zero sheer viscosity of copolymer/DEF solution increased with an increase in the polymer content of the solution. (See, Table 7; FIG. 30) The zero sheer viscosity of the 70 % polymer solutions were found to be in the 3D printable range of around 2 Pa·s. (See also, Tables 7A-7R in Appendix A)

Comparative Example 5

*10%, DP 10 Poly(propylene fumarate-co-succinate) Copolymer Synthesis
Maleic Anhydride and Succinic anhydride added before the Initiating Alcohol*

[00140] A DP 10 polymer with a 10 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Comparative Example 1, except that 2.524 g of maleic anhydride, 0.286 g of succinic anhydride and 348 mg of $\text{Mg}(\text{BHT})_2(\text{THF})_2$ are mixed first, and then 8.2 mL of toluene, 165 μL of propargyl alcohol and 2 mL of propylene oxide were added. After the purification process, 3.8 g of polymer was collected. 1 g of obtained polymer was isomerized following procedures used in Comparative Example 3, above, and the trans polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 19.9H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 13.0H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.54 (m, 2H, CCH_2O), 4.40-3.98 (m, 30.8H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 5.1H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.0H, CHC), 1.40-0.98 (m, 49.5, CHCH_3). (See FIG. 31) The DP that calculated by NMR is 13 and succinate content is 11%.

Comparative Example 6

*10%, DP 20 Poly(propylene fumarate-co-succinate) Copolymer Synthesis
Maleic Anhydride and Succinic anhydride added before the Initiating Alcohol*

[00141] A DP 20 polymer with a 10 mol% succinic anhydride feed ratio was synthesized following same procedure shown in Example 18, except that 83 μL of propargyl alcohol were added. After the purification process, 3.9 g of polymer was collected. 1 g of obtained polymer was isomerized following procedures used in Comparative Example 3, above, and the trans polymer was recovered. The resulting copolymer was characterized by ^1H NMR ((300 MHz, 298 K, CDCl_3): 6.99-6.76 (m, 30.7H, $\text{C}=\text{OCHCHC}=\text{O}$), 5.36-5.05 (m, 19.4H, $\text{CH}_2\text{CHCH}_3\text{O}$), 4.80-4.54 (m, 2H, CCH_2O),

4.40-3.98 (m, 44.12H, $\text{OCH}_2\text{CHCH}_3$), 2.73-2.56 (m, 5.9H, $\text{OCH}_2\text{CHCH}_3$), 2.56-2.49 (m, 1.0H, CHC), 1.40-0.98 (m, 73.0, CHCH_3). (See FIG. 32) The DP that calculated by NMR is 19 and succinate content is 9%.

Example 20

Comparative Absorbance of the Trans Copolymers

[00142] The absorbance of the PPF (trans) copolymers produced in Comparative Examples 3-6, and in Examples 9-12 and 14-16 were measured in 1 % THF solution using a BioTek Synergy Mx microplate reader, as set forth above. The absorbance at 360 and 405 nm is summarized in Table 8, below.

Table 8
*Absorbance Results for Examples 9-12, 14-16,
and Comparative Examples 3-6*

Entry	DP	Composition (Mol%)		Absorbance	
		Fm	SAn	360 nm	405 nm
C. Example 3	10	100	0	0.028	0.039
C. Example 4	20	100	0	0.035	0.017
C. Example 5	10	89	11	1.747	1.090
C. Example 6	20	91	9	1.797	1.103
Example 9	10	89	11	0.069	0.036
Example 10	10	80	20	0.076	0.045
Example 11	20	90	10	0.112	0.066
Example 12	20	85	15	0.167	0.101
Example 14	6	76	24	0.043	0.026
Example 15	10	84	16	0.319	0.187
Example 16	11	74	26	0.069	0.036

[00143] As can be seen, the polymers made by adding the maleic anhydride and succinic anhydride before the initiating alcohol (Comparative Examples 5 and 6) both have much higher absorbance in 360nm and 405 nm wavelength of photo initiator, than do the other polymers (Comparative Examples 3 and 4 and Examples 9-12, 14-16) where the initiating alcohol was added before the maleic anhydride or succinic anhydride. Moreover, all of these polymers (Comparative Examples 3 and 4 and Examples 9-12, 14-16) have an absorbance at the wavelength ranges of the photo initiator (from about 360

nm and about 405 nm) low enough that their absorbance does not substantially interfere with the 3D printing process. This is true without respect to the presence of succinic anhydride in the polymer as can be seen by comparing the absorbance of polymers of Comparative Examples 3 and 4 to the absorbance of the polymers of Comparative 5 and 6.

Example 21

Characterization and analysis of the effects of the order of addition on polymer absorbance

Characterization techniques

[00144] Proton (^1H) NMR experiments were performed in CDCl_3 at 25 °C using a Varian Mercury 300 spectrometer. All chemical shifts were recorded in parts per million (ppm) relative to the reference peak solvent: chloroform at $\delta = 7.26$.

[00145] The dispersities ($\bar{D}$) of polymers were determined by size exclusion chromatography (SEC) on a Tosoh EcoSEC HLC-8320GPC with TSKgel GMHHR-M columns in series. The detector used in this determination is a refractive index detector. Dimethylformamide (DMF) was used as eluent ($0.2 \text{ mL}\cdot\text{min}^{-1}$) at 40 °C in the presence of LiBr ($1 \text{ g}\cdot\text{L}^{-1}$). Molecular masses were calculated through a calibration curve determined from polystyrene standards. The sample concentration is $10 \text{ mg}\cdot\text{mL}^{-1}$.

[00146] Rheological information was obtained using an ARES-G2 rheometer using a 50 mm diameter parallel plate flow cell with a geometry gap of 0.3 mm with environmental conditions set to 25 °C. The temperature was controlled with a Peltier system. Oscillatory shear measurements were done in the linear response regime. Samples were loaded onto the rheometer, and it was verified that the system was stable before the frequency dependence of the storage (G'), loss (G'') moduli and the zero-shear viscosity η_0 . (See Tables 12-13 in Appendix B.)

Kinetic studies

[00147] Kinetic studies of the ring opening copolymerization (ROCOP) of maleic anhydride (MAN) and propylene oxide (PO) using propargyl alcohol (PrOH) as initiator were performed to investigate the influence of the order of addition of the reactive

species. In both cases, the total target DP was 20, and the molar ratios were $[\text{MAN}]_0 : [\text{PO}]_0 : [\text{PrOH}]_0 : [\text{Cat.}]_0 = 20 : 20 : 1 : 0.2$, corresponding to 5 g of MAN (5.10×10^{-2} mol), 3.6 mL of PO (5.10×10^{-2} mol), 0.147 mL of PrOH (2.55×10^{-3} mol) and 0.308 mg of catalyst (5.10×10^{-4} mol). The total monomer concentration was 7 M. (See, Tables 9-11 in Appendix B)

[00148] For kinetic studies, the mixture was split in several vials, immersed in a preheated bath at 80 °C (corresponding to the time zero of the reaction), polymerizations were conducted under stirring and stopped by cooling down to ambient temperature and by adding an excess of chloroform. The monomer conversions were determined by ^1H NMR in CDCl_3 of crude samples from reactional volumes and the dispersity by DMF GPC after precipitation in diethyl ether and drying. (See, Tables 9-11 in Appendix B)

Discussion

[00149] Due to the huge influence of the order of addition of the reactive species on the color of the final polymer obtained, the possible impact on the kinetic of polymerization as well as the polymerization process as investigated. Various aliquots of crude product were analyzed by ^1H NMR at different polymerization times to calculate the conversion of the MAN monomer and the $\ln([M_0]/[M_t])$ values and the SEC in DMF provided the dispersity over time. (See, Table 9 in Appendix B)

[00150] FIGS. 33A-C show the evolution of the $\ln([M_0]/[M_t])$ values and the conversion of MAN with time respectively. For the first order of addition (black triangle, corresponding to the addition of Man and catalyst first), the kinetics plots revealed a slow initiation step followed by a faster polymerization step undergoing a drastic slowdown after 22 hrs, corresponding to only 81 % of conversion. Despite 50 hrs of polymerization, the maximum of conversion was 85 %. Moreover, although FIG. 33C shows a linear molar mass growth over the polymerization, the dispersity value ranged from 2.1 at 58 % of conversion to 1.45 at 85 %, supporting the idea of a slow and inhomogeneous initiation step leading to various populations of growing chains.

[00151] On the contrary, the kinetic plots corresponding to the couple catalyst + alcohol (circles on FIG. 33A), revealed a linear pseudo-first order behavior with an initiation step as fast as the polymerization step which is characteristic of a constant concentration of propagating species during the polymerization.

[00152] As a consequence of the pseudo-first order kinetics, it can be assumed that the number of active chains is maintained and no termination side reactions occur throughout the polymerization. Linear molar mass growth and the dispersity stayed low during the polymerization (FIG. 33D), providing further evidence of controlled ROCOP. In addition, the final conversion reached after 52 hrs of polymerization was 95 %, 10 % higher than previously.

[00153] The traces indicate very different polymerization kinetics. Indeed, the calculated propagation constants $k_{\text{Cat+Man}}$ and $k_{\text{Cat+PrOH}}$ corresponding to the couples Catalyst+MAN (maleic anhydride added before the propargyl alcohol) and Catalyst+alcohol (propargyl alcohol added before the maleic anhydride), respectively are $5.88 \times 10^{-5} \text{ L.mol}^{-1}.\text{s}^{-1}$ and $2.34 \times 10^{-5} \text{ L.mol}^{-1}.\text{s}^{-1}$ (see, the linear part of the graphs in FIGS. 33A-B). As a consequence, the polymerization results in the formation of a polymer that is less polydispersed, with a higher conversion, and a lighter color (lower absorbance), but takes nearly twice as long.

[00154] This information is of primary importance, on the one hand in order to synthesize polymers of controlled molar mass and in a reproducible manner and on the other hand to develop a scale up protocol.

[00155] In order to measure the complex viscosity of the printable resins and to investigate the differences between the clear and the dark polypropylene fumarate (PPF, $\overline{M}_n = 3 \text{ KDa}$, DP 20), the polymers were mixed with diethyl fumarate (DEF) to reach 50:50 and 60:40 (PPF:DEF) weight ratios. (See Tables 12-13 in Appendix B)

[00156] FIGS. 34A-B show the evolutions of the complex viscosity with the angular frequency of the resin based on dark and clear PPF respectively. Regarding the dark PPF, the complex viscosity values are 2.4 and 0.5 Pa.s for PPF:DEF ratios of 60:40 and 50:50 respectively while they are equal to 1.60 and 0.5 Pa.s for the clear PPF. These results

suggest that both formulations have very similar rheological properties, even if the light PPF-based resin (60:40) seems to be slightly less viscous than its darker counterpart.

[00157] In light of the foregoing, it should be appreciated that the present invention significantly advances the art by providing a PPF-based 3D-printable polymer that is structurally and functionally improved in a number of ways. While particular embodiments of the invention have been disclosed in detail herein, it should be appreciated that the invention is not limited thereto or thereby inasmuch as variations on the invention herein will be readily appreciated by those of ordinary skill in the art. The scope of the invention shall be appreciated from the claims that follow.

APPENDIX A

(THE TABLES IN THIS APPENDIX ARE COMPLEMENTARY OF TABLE 7)

Table 7A*Summary of Complex Viscosity Results for Example 14*

Example 14					
Angular frequency (rad/s)	Complex viscosity (Pa.s)				
	50%	70%	80%	90%	100 %
0.5	0.206537	1.61805	9.2989	43.4254	1099.19
0.629463	0.105637	1.57993	9.93337	43.8326	1082.6
0.792447	0.149983	1.57747	9.58983	43.9737	1079.13
0.997631	0.10604	1.58106	9.60137	44.1576	1078.11
1.25594	0.105959	1.60365	9.71661	43.7502	1078.5
1.58114	0.103188	1.59298	9.66137	43.7588	1080.32
1.99054	0.10435	1.59765	9.50725	43.0833	1082
2.50594	0.124924	1.58682	9.47201	43.4411	1082.84
3.15479	0.107352	1.59131	9.70096	43.2462	1083.81
3.97164	0.112914	1.59563	9.69355	43.0501	1084.49
5	0.116272	1.59964	9.59834	42.8438	1084.36
6.29463	0.118903	1.59413	9.63991	42.8354	1086.22
7.92447	0.116895	1.59508	9.60374	42.7852	1088.27
9.97631	0.118496	1.59333	9.605	42.73	1089.06
12.5594	0.120124	1.59194	9.59835	42.638	1089.52
15.8114	0.11881	1.59259	9.62414	42.611	1094.34
19.9054	0.118605	1.59164	9.59596	42.5609	1094.03
25.0594	0.120536	1.58528	9.60065	42.5313	1094.01
31.5479	0.118694	1.59037	9.61612	42.4953	1093.68
39.7164	0.118403	1.58943	9.62499	42.4547	1092.83
50	0.119006	1.58953	9.63018	42.439	1091.24
62.9463	0.119122	1.58815	9.63468	42.4197	1083.18
79.2447	0.120101	1.58757	9.64316	42.3993	1079.81
100	0.118058	1.58187	9.65312	42.3872	1075.98

Table 7B
Complex Viscosity Results for Example 14 at 50% Polymer Content

Example 14 (50% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	23.747	9.96326	0.010289	6.29864	0.016193	0.101991	0.206537
0.629463	45.1432	23.747	9.96139	6.62E-03	-26.8342	-2.48E-03	0.066448	0.105637
0.792447	61.0327	23.741	9.95845	0.011836	18.9525	6.26E-03	0.118688	0.149983
0.997631	73.6617	23.736	9.95808	0.010535	-13.4739	-7.83E-03	0.105499	0.10604
1.25594	83.7063	23.736	9.96121	0.013256	4.41149	0.02942	0.129786	0.105959
1.58114	91.69	23.733	9.95875	0.016248	6.5605	0.024585	0.161291	0.103188
1.99054	98.039	23.73	9.95623	0.02068	-16.6851	-0.01243	0.207341	0.10435
2.50594	103.084	23.727	9.96032	0.031181	15.3363	0.020369	0.312388	0.124924
3.15479	107.097	23.722	9.95678	0.033721	61.4164	5.51E-03	0.338626	0.107352
3.97164	110.298	23.725	9.9571	0.044653	-20.4784	-0.02187	0.447921	0.112914
5	112.841	23.728	9.96169	0.057913	-31.95	-0.01819	0.581076	0.116272
6.29463	121.889	23.725	9.95648	0.074518	111.798	6.69E-03	0.748423	0.118903
7.92447	129.092	23.724	9.95662	0.092229	-70.2543	-0.01318	0.926235	0.116895
9.97631	134.808	23.718	9.95781	0.117712	136.61	8.65E-03	1.18212	0.118496
12.5594	139.869	23.719	9.95819	0.150229	-308.139	-4.90E-03	1.50868	0.120124
15.8114	147.137	23.715	9.95518	0.186995	161.102	0.011661	1.87852	0.11881
19.9054	153.512	23.716	9.95377	0.23496	89.3931	0.026409	2.36073	0.118605
25.0594	158.861	23.711	9.95011	0.300476	-56.1392	-0.0538	3.02007	0.120536
31.5479	170.227	23.709	9.94347	0.372191	57.8437	0.064726	3.74398	0.118694
39.7164	176.806	23.709	9.93369	0.466843	60.5806	0.077614	4.70189	0.118403
50	182.468	23.705	9.91817	0.589584	46.4806	0.127988	5.94895	0.119006
62.9463	190.444	23.704	9.89398	0.740729	45.5858	0.164448	7.4965	0.119122
79.2447	197.254	23.704	9.85816	0.935962	29.9751	0.317331	9.51204	0.120101
100	202.603	23.708	9.80406	1.15282	-114.379	-0.10321	11.8053	0.118058

Table 7C
Complex Viscosity Results for Example 14 at 70% Polymer Content

Example 14 (70% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1403	23.662	9.96332	0.080606	-465.933	-1.74E-03	0.809022	1.61805
0.629463	45.1452	23.66	9.96155	0.099069	-682.868	-1.46E-03	0.994508	1.57993

0.792447	61.0348	23.656	9.95799	0.124481	-26.3248	-0.04745	1.24916	1.57747
0.997631	73.6642	23.654	9.95803	0.157069	-160.926	-9.80E-03	1.57728	1.58106
1.25594	83.7065	23.65	9.96139	0.200632	209.936	9.59E-03	2.01407	1.60365
1.58114	91.6883	23.653	9.9586	0.250829	-44.4785	-0.05661	2.51808	1.59298
1.99054	98.0362	23.653	9.95632	0.316628	-301.083	-0.01056	3.18016	1.59765
2.50594	103.084	23.647	9.96026	0.396066	-200.169	-0.01987	3.97642	1.58682
3.15479	107.097	23.647	9.95705	0.499869	2022.5	2.48E-03	5.02025	1.59131
3.97164	110.298	23.647	9.95668	0.63098	-727.46	-8.71E-03	6.33725	1.59563
5	112.841	23.645	9.96161	0.79675	194.05	0.041217	7.9981	1.59964
6.29463	124.883	23.638	9.95636	0.999066	226.255	0.04435	10.0344	1.59413
7.92447	132.872	23.639	9.9567	1.25855	244.183	0.051765	12.6401	1.59508
9.97631	138.586	23.639	9.9577	1.58283	227.014	0.070019	15.8954	1.59333
12.5594	143.646	23.641	9.95835	1.99106	197.77	0.101095	19.9936	1.59194
15.8114	151.321	23.642	9.95496	2.50677	185.671	0.13562	25.1807	1.59259
19.9054	157.694	23.635	9.95405	3.15366	260.542	0.1216	31.6819	1.59164
25.0594	163.042	23.635	9.95008	3.95278	188.635	0.210595	39.7255	1.58528
31.5479	174.806	23.632	9.94352	4.98892	217.429	0.230752	50.1721	1.59037
39.7164	181.217	23.628	9.93356	6.2707	193.589	0.326081	63.1258	1.58943
50	186.632	23.626	9.91838	7.88273	185.794	0.42776	79.4752	1.58953
62.9463	194.5	23.628	9.89427	9.89105	185.625	0.538541	99.9669	1.58815
79.2447	201.393	23.619	9.85822	12.4021	121.493	1.03547	125.802	1.58757
100	208.876	23.618	9.80429	15.5088	99.3293	1.59247	158.179	1.58187

Table 7D
Complex Viscosity Results for Example 14 at 80% Polymer Content

Example 14 (80% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	24.953	9.9626	0.463206	44.2805	0.104973	4.64826	9.2989
0.629463	45.1453	24.952	9.96143	0.622857	26.6675	0.234304	6.24829	9.93337
0.792447	61.0352	24.96	9.95864	0.7568	-48.3025	-0.1573	7.5978	9.58983
0.997631	73.6642	24.971	9.95827	0.953866	-1332.29	-7.19E-03	9.57862	9.60137
1.25594	83.7087	24.982	9.96164	1.21567	-59.7533	-0.2042	12.2018	9.71661
1.58114	91.6925	24.987	9.95883	1.52131	-107.437	-0.14218	15.2753	9.66137
1.99054	98.0415	24.993	9.95657	1.88423	-37.1284	-0.50952	18.9177	9.50725
2.50594	103.087	24.995	9.96052	2.36425	76.1784	0.311561	23.7342	9.47201
3.15479	107.099	24.994	9.95694	3.04727	40.7368	0.751046	30.5952	9.70096
3.97164	110.3	25.001	9.95682	3.83331	51.6537	0.745193	38.4921	9.69355
5	112.844	25.004	9.96191	4.78089	-140.146	-0.34243	47.9905	9.59834

6.29463	121.891	25.006	9.95654	6.04159	170.617	0.355641	60.6786	9.63991
7.92447	129.094	25.01	9.95683	7.5776	212.241	0.358571	76.1037	9.60374
9.97631	134.81	25.009	9.95784	9.54185	166.156	0.576686	95.8207	9.605
12.5594	139.871	25.011	9.95856	12.005	232.045	0.519509	120.549	9.59835
15.8114	147.14	25.015	9.95526	15.149	162.07	0.938906	152.168	9.62414
19.9054	153.514	25.011	9.95416	19.0135	231.411	0.825412	191.009	9.59596
25.0594	158.864	25.015	9.95037	23.9392	398.97	0.603017	240.585	9.60065
31.5479	166.445	25.011	9.9441	30.1672	270.419	1.12184	303.366	9.61612
39.7164	176.812	25.012	9.9347	37.9774	285.942	1.33687	382.268	9.62499
50	182.986	25.01	9.91929	47.7623	315.816	1.52464	481.507	9.63018
62.9463	192.657	25.004	9.89548	60.0129	295.459	2.05261	606.464	9.63468
79.2447	202.01	25.001	9.86001	75.3471	274.597	2.78285	764.164	9.64316
100	209.996	25.004	9.80579	94.6564	701.175	1.37666	965.311	9.65312

Table 7E

Complex Viscosity Results for Example 14 at 90% Polymer Content

Example 14 (90% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1403	24.966	9.96281	2.1632	44.6958	0.485666	21.7073	43.4254
0.629463	45.1432	24.968	9.96156	2.74849	36.944	0.74656	27.5809	43.8326
0.792447	61.0328	24.976	9.95843	3.47019	477.15	0.073031	34.8467	43.9737
0.997631	73.6618	24.978	9.95806	4.38683	316.197	0.139321	44.0528	44.1576
1.25594	83.7065	24.979	9.96154	5.47364	47.4399	1.158	54.9355	43.7502
1.58114	91.6902	24.985	9.95894	6.89046	85.86	0.805778	69.184	43.7588
1.99054	98.0392	24.99	9.95641	8.53851	121.47	0.705986	85.756	43.0833
2.50594	103.084	24.999	9.96063	10.8432	50.3622	2.16113	108.839	43.4411
3.15479	107.096	24.997	9.9571	13.5847	68.5695	1.98948	136.418	43.2462
3.97164	110.298	24.996	9.95683	17.0241	77.9911	2.19212	170.965	43.0501
5	112.842	24.998	9.96199	21.3405	149.766	1.43033	214.214	42.8438
6.29463	121.888	25.003	9.9566	26.8463	87.7086	3.07399	269.615	42.8354
7.92447	129.091	25.002	9.95709	33.7595	82.9213	4.08852	339.025	42.7852
9.97631	134.807	25.007	9.95802	42.4499	99.6953	4.27571	426.267	42.73
12.5594	139.869	25.011	9.95906	53.3316	107.292	4.99092	535.486	42.638
15.8114	147.137	25.008	9.95579	67.076	113.629	5.92906	673.713	42.611
19.9054	153.512	25.006	9.95504	84.3382	125.028	6.77581	847.163	42.5609
25.0594	158.861	25.007	9.95196	106.069	135.976	7.83797	1065.78	42.5313
31.5479	166.442	25.011	9.94649	133.346	142.813	9.38716	1340.6	42.4953
39.7164	172.854	25.003	9.93747	167.561	151.681	11.1162	1686.11	42.4547

50	178.27	25.008	9.92333	210.568	164.578	12.893	2121.91	42.439
62.9463	186.137	25.011	9.9008	264.367	179.293	14.8925	2670.12	42.4197
79.2447	193.031	25.003	9.86558	331.475	194.735	17.2535	3359.87	42.3993
100	198.377	25.002	9.81267	415.932	219.782	19.2859	4238.68	42.3872

Table 7F

Complex Viscosity Results for Example 14 at 100% Polymer Content

Example 14 (100% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	25.02	9.96623	54.774	146.611	3.74856	549.583	1099.19
0.629463	45.1492	25.064	9.9628	67.8922	182.064	3.74291	681.447	1082.6
0.792447	61.043	25.076	9.95856	85.161	182.115	4.69561	855.141	1079.13
0.997631	73.6762	25.076	9.95809	107.105	214.346	5.01782	1075.55	1078.11
1.25594	83.7225	25.07	9.96115	134.927	252.495	5.36453	1354.52	1078.5
1.58114	91.7083	25.057	9.95874	170.109	252.252	6.77147	1708.12	1080.32
1.99054	98.0572	25.055	9.95647	214.438	268.721	8.01479	2153.74	1082
2.50594	103.104	25.044	9.96054	270.283	278.832	9.73171	2713.52	1082.84
3.15479	107.119	25.042	9.9578	340.475	274.849	12.4401	3419.16	1083.81
3.97164	110.314	25.036	9.95815	428.917	270.445	15.9262	4307.17	1084.49
5	112.863	25.035	9.96401	540.228	256.181	21.1637	5421.75	1084.36
6.29463	121.915	25.024	9.95924	680.948	235.081	29.0848	6837.29	1086.22
7.92447	129.113	25.016	9.96203	859.122	213.903	40.3168	8623.87	1088.27
9.97631	135.454	25.006	9.9658	1082.76	188.614	57.6017	10864.6	1089.06
12.5594	140.51	25.006	9.97178	1364.52	164.427	83.2197	13683.6	1089.52
15.8114	148.182	24.992	9.97519	1726.01	145.576	118.857	17302.7	1094.34
19.9054	154.554	24.99	9.985	2174.44	124.438	174.998	21776.4	1094.03
25.0594	159.901	24.99	9.99715	2740.73	103.908	263.828	27413.8	1094.01
31.5479	167.482	24.991	10.0126	3454.67	87.4343	394.593	34501	1093.68
39.7164	174.053	24.984	10.0305	4353.59	73.6646	589.147	43399.3	1092.83
50	179.469	24.987	10.0479	5482.35	62.1382	877.965	54555.1	1091.24
62.9463	187.336	24.983	10.0568	6856.93	50.6754	1345.21	68169	1083.18
79.2447	194.232	24.985	10.0467	8596.95	42.9472	1991.9	85546.3	1079.81
100	199.591	24.983	10.004	10738.6	36.3838	2949.19	107303	1075.98

Table 7G
Summary of Complex Viscosity Results for Example 15

Example 15					
Angular frequency rad/s	Complex viscosity (Pa.s)				
	50%	70%	80%	90%	100%
0.5	0.576713	2.64267	14.1969	104.995	3483.12
0.629463	0.509636	2.04439	14.2707	105.351	3489.88
0.792447	0.43278	2.2029	14.1946	105.858	3498.43
0.997631	0.169537	2.08915	14.2979	106.421	3501.32
1.25594	0.352566	2.26548	14.4085	106.247	3501.68
1.58114	0.215948	2.3589	14.1949	106.372	3501.42
1.99054	0.16773	2.15981	14.3301	106.887	3501.04
2.50594	0.134944	2.373	14.359	106.442	3500.42
3.15479	0.157384	2.30637	14.3765	106.591	3501.55
3.97164	0.145471	2.38015	14.4181	106.424	3497.81
5	0.197265	2.31008	14.3651	106.519	3491.95
6.29463	0.184135	2.30146	14.3429	106.54	3488.93
7.92447	0.157583	2.30527	14.337	106.587	3484.67
9.97631	0.15041	2.33055	14.3484	106.501	3477.3
12.5594	0.160743	2.34845	14.3 533	106.446	3469.2
15.8114	0.161701	2.32513	14.3416	106.429	3458.62
19.9054	0.153346	2.31382	14.3138	106.369	3446.06
25.0594	0.149633	2.32941	14.3073	106.303	3429.39
31.5479	0.142733	2.32251	14.3149	106.223	3409.39
39.7164	0.146433	2.32987	14.3081	106.168	3384.36
50	0.153585	2.32078	14.3086	106.094	3354.4
62.9463	0.148835	2.32678	14.3028	105.99	3315.03
79.2447	0.146862	2.32716	14.2987	105.898	3269.32
100	0.151412	2.334	14.3087	105.747	3213.04

Table 7H
Complex Viscosity Results for Example 15 at 50% Polymer Content

Example 15 (50% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	25.129	9.96138	0.028724	-0.72447	-0.23352	0.169175	0.576713
0.629463	45.1432	25.054	9.95959	0.03195	0.616849	0.273031	0.168418	0.509636

0.792447	61.033	25.004	9.95686	0.034148	-0.37477	-0.32114	0.120356	0.43278
0.997631	73.6622	24.971	9.95717	0.016841	-0.01078	-0.16913	1.82E-03	0.169537
1.25594	83.7067	24.95	9.96062	0.044106	1.3374	0.265164	0.35463	0.352566
1.58114	91.6903	24.941	9.95874	0.034004	-2.56157	-0.12417	0.318066	0.215948
1.99054	98.0393	24.937	9.95598	0.03324	1.56508	0.179765	0.281346	0.16773
2.50594	103.085	24.938	9.96053	0.033683	-1.45199	-0.19181	0.2785	0.134944
3.15479	107.097	24.937	9.95681	0.049437	47.0542	0.01055	0.496401	0.157384
3.97164	110.298	24.934	9.95697	0.057527	1.40956	0.3343	0.471218	0.145471
5	112.842	24.938	9.96172	0.098255	0.932397	0.721395	0.672627	0.197265
6.29463	128.876	24.951	9.95673	0.115404	-4.34492	-0.25997	1.12953	0.184135
7.92447	136.079	24.96	9.95703	0.124338	6.52658	0.189127	1.23435	0.157583
9.97631	141.794	24.962	9.95783	0.149418	-6.54899	-0.2265	1.48335	0.15041
12.5594	148.857	24.974	9.95867	0.201043	-17.8851	-0.1127	2.0157	0.160743
15.8114	162.093	24.989	9.95536	0.254518	-25.489	-0.10023	2.55476	0.161701
19.9054	168.464	24.987	9.95388	0.303806	-43.385	-0.07034	3.05161	0.153346
25.0594	173.81	25	9.9503	0.373049	-100.753	-0.03721	3.74952	0.149633
31.5479	181.39	25	9.94379	0.447639	30.8002	0.14612	4.50054	0.142733
39.7164	187.968	25.009	9.93391	0.577499	207.531	0.028023	5.81571	0.146433
50	193.378	25.011	9.91829	0.761205	154.682	0.049645	7.67911	0.153585
62.9463	201.553	25.013	9.89426	0.926035	53.6028	0.174748	9.36697	0.148835
79.2447	208.363	25.012	9.85821	1.14545	31.8717	0.364972	11.6323	0.146862
100	213.712	25.018	9.80426	1.48089	30.8936	0.489851	15.1333	0.151412

Table 7I
Complex Viscosity Results for Example 15 at 70% Polymer Content

Example 15 (70% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	25.028	9.96205	0.131632	-9.73647	-0.135	1.31442	2.64267
0.629463	55.125	24.986	9.96057	0.12818	24.73	0.051994	1.28582	2.04439
0.792447	71.0203	24.976	9.95784	0.173832	-21.8909	-0.07966	1.74386	2.2029
0.997631	83.6513	24.974	9.95792	0.207544	14.3592	0.144797	2.07917	2.08915
1.25594	98.6997	24.976	9.96136	0.283432	-54.3262	-0.05237	2.84484	2.26548
1.58114	110.657	24.975	9.95872	0.371435	-366.965	-0.01016	3.72974	2.3589
1.99054	117.007	24.982	9.95672	0.428058	-19.396	-0.22136	4.29348	2.15981
2.50594	122.052	24.983	9.96014	0.592289	67.7563	0.087755	5.94595	2.373
3.15479	126.065	24.985	9.95701	0.724482	27.4708	0.264691	7.27128	2.30637
3.97164	129.266	24.985	9.95699	0.941245	42.4282	0.222741	9.45049	2.38015
5	131.811	24.985	9.96173	1.15062	-45.4403	-0.25413	11.5476	2.31008

6.29463	140.858	24.994	9.95664	1.4424	749.676	0.019324	14.4868	2.30146
7.92447	148.061	24.993	9.95673	1.8189	789.172	0.023148	18.268	2.30527
9.97631	153.777	24.993	9.95759	2.31517	487.464	0.047696	23.2502	2.33055
12.5594	158.838	24.996	9.95855	2.93729	73.0379	0.403796	29.4924	2.34845
15.8114	169.683	25	9.95498	3.65981	598.133	0.061464	36.7635	2.32513
19.9054	176.056	25.003	9.95425	4.58468	-2221.93	-0.02073	46.0575	2.31382
25.0594	181.404	25.006	9.95017	5.80826	857.763	0.068053	58.3735	2.32941
31.5479	188.985	25.005	9.94378	7.28582	366.256	0.200051	73.27	2.32251
39.7164	195.396	25.007	9.93399	9.1923	375.402	0.246496	92.5336	2.32987
50	202.821	25.007	9.91842	11.5092	254.595	0.455774	116.038	2.32078
62.9463	211.094	25.005	9.89433	14.4914	412.001	0.35549	146.462	2.32678
79.2447	217.903	25.003	9.85845	18.1804	317.525	0.580787	184.414	2.32716
100	223.252	25.007	9.80469	22.884	147.038	1.58731	233.395	2.334

Table 7J

Complex Viscosity Results for Example 15 at 80% Polymer Content

Example 15 (80% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	25.063	9.96343	0.707248	-37.4613	-0.18942	7.0959	14.1969
0.629463	45.1452	25.046	9.96077	0.894763	-36.8176	-0.24389	8.97956	14.2707
0.792447	61.0348	25.02	9.95736	1.12005	-227.682	-0.0494	11.2483	14.1946
0.997631	73.6642	25.003	9.95773	1.42037	-133.989	-0.10645	14.2636	14.2979
1.25594	83.7065	24.99	9.96122	1.80261	561.387	0.032235	18.0963	14.4085
1.58114	91.6883	24.988	9.95864	2.23513	5590.04	4.02E-03	22.4441	14.1949
1.99054	98.0363	24.979	9.95631	2.83999	83.6023	0.341169	28.5225	14.3301
2.50594	103.084	24.982	9.96043	3.58403	260.931	0.1379	35.9824	14.359
3.15479	107.097	24.978	9.95677	4.51589	65.907	0.688086	45.3497	14.3765
3.97164	110.298	24.979	9.95666	5.70155	191.924	0.298364	57.2629	14.4181
5	112.841	24.979	9.96181	7.15511	182.305	0.393978	71.8243	14.3651
6.29463	121.889	24.977	9.95653	8.98906	195.179	0.462559	90.2819	14.3429
7.92447	129.093	24.979	9.9568	11.3122	181.839	0.62479	113.611	14.337
9.97631	134.808	24.978	9.95769	14.2539	204.85	0.698765	143.143	14.3484
12.5594	139.87	24.981	9.95866	17.9524	189.964	0.948964	180.267	14.3533
15.8114	147.138	24.983	9.95527	22.5746	249.655	0.908286	226.758	14.3416
19.9054	153.513	24.985	9.95448	28.3624	246.5	1.15585	284.918	14.3138
25.0594	158.862	24.989	9.95076	35.6767	209.015	1.71532	358.528	14.3073
31.5479	166.444	24.991	9.94453	44.91	217.114	2.08002	451.601	14.3149
39.7164	173.962	24.99	9.93513	56.4582	215.613	2.63557	568.262	14.3081

50	179.381	24.997	9.91982	70.9692	212.99	3.35893	715.421	14.3086
62.9463	190.645	24.996	9.89649	89.0992	233.986	3.84767	900.302	14.3028
79.2447	200.863	25.003	9.86082	111.733	261.256	4.33709	1133.09	14.2987
100	207.596	25.002	9.80689	140.324	288.261	4.96376	1430.86	14.3087

Table 7K
Complex Viscosity Results for Example 15 at 90% Polymer Content

Example 15 (90% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	37.7068	25.038	9.96194	5.22976	422.583	0.124229	52.4973	104.995
0.629463	57.7088	25.014	9.96125	6.60577	1185.06	0.055962	66.3146	105.351
0.792447	73.5965	24.993	9.9576	8.35314	274.651	0.305429	83.8866	105.858
0.997631	86.2315	24.986	9.9578	10.572	274.525	0.386732	106.168	106.421
1.25594	96.2693	24.979	9.96133	13.2924	246.66	0.540985	133.439	106.247
1.58114	104.25	24.977	9.95897	16.7499	262.507	0.6407	168.188	106.372
1.99054	110.597	24.976	9.95573	21.1819	201.683	1.05492	212.759	106.887
2.50594	115.64	24.976	9.96073	26.5691	240.528	1.10896	266.736	106.442
3.15479	119.651	24.979	9.95735	33.4839	243.714	1.37977	336.27	106.591
3.97164	122.851	24.976	9.95653	42.084	196.197	2.15432	422.672	106.424
5	125.395	24.975	9.96192	53.0565	229.668	2.31895	532.589	106.519
6.29463	134.442	24.978	9.9572	66.7756	251.27	2.66893	670.621	106.54
7.92447	144.807	24.987	9.957	84.1015	232.953	3.62579	844.639	106.587
9.97631	150.523	24.988	9.95878	105.811	227.18	4.6768	1062.48	106.501
12.5594	155.575	24.986	9.95961	133.151	197.905	6.75519	1336.89	106.446
15.8114	163.243	24.99	9.95692	167.554	188.576	8.92356	1682.77	106.429
19.9054	169.612	24.987	9.95752	210.831	174.037	12.1656	2117.27	106.369
25.0594	174.956	24.994	9.95426	265.169	151.311	17.6049	2663.82	106.303
31.5479	182.533	24.997	9.95108	333.473	136.359	24.5751	3351.03	106.223
39.7164	189.427	24.997	9.94341	419.275	122.263	34.4869	4216.47	106.168
50	194.845	24.999	9.93118	526.82	109.854	48.2869	5304.48	106.094
62.9463	202.715	25.004	9.91057	661.199	98.6181	67.6479	6671.31	105.99
79.2447	209.61	25.005	9.87696	828.857	89.2571	94.0127	8391.3	105.898
100	214.957	25.004	9.82528	1038.99	80.089	132.026	10573.8	105.747

Table 7L

Complex Viscosity Results for Example 15 at 100% Polymer Content

Example 15 (100% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1407	25.006	9.96327	173.516	155.088	11.2293	1741.53	3483.12
0.629463	45.1493	24.992	9.96147	218.828	175.618	12.5085	2196.71	3489.88
0.792447	61.0432	24.986	9.95846	276.08	223.149	12.4235	2772.29	3498.43
0.997631	73.6765	24.986	9.95778	347.828	163.708	21.3365	3492.96	3501.32
1.25594	83.7227	24.986	9.96144	438.095	213.62	20.5874	4397.86	3501.68
1.58114	91.7087	24.986	9.9587	551.337	148.709	37.2278	5536.11	3501.42
1.99054	98.0573	24.99	9.95622	693.843	110.242	63.2124	6968.65	3501.04
2.50594	103.104	24.991	9.96039	873.709	98.8727	88.7139	8771.38	3500.42
3.15479	107.119	24.995	9.95709	1099.93	84.1289	131.297	11045.9	3501.55
3.97164	111.896	24.991	9.95679	1383.2	79.1645	175.469	13890.9	3497.81
5	114.445	24.993	9.9618	1739.31	67.265	259.538	17457.8	3491.95
6.29463	123.497	24.994	9.95659	2186.62	54.5725	402.361	21957.8	3488.93
7.92447	130.695	24.996	9.95711	2749.57	46.6438	591.887	27607.8	3484.67
9.97631	136.407	24.997	9.95779	3454.42	39.3934	880.337	34679.5	3477.3
12.5594	141.466	24.999	9.95911	4339.31	33.2772	1308.75	43551.6	3469.2
15.8114	149.141	24.994	9.95544	5444.19	28.0172	1950.62	54650.8	3458.62
19.9054	155.515	24.997	9.95504	6828.67	23.7531	2885.28	68534.4	3446.06
25.0594	160.864	24.999	9.95153	8552.19	20.1318	4263.54	85832.6	3429.39
31.5479	168.446	25.003	9.94585	10697.7	17.1627	6256.4	107377	3409.39
39.7164	175.017	25	9.937	13356.8	14.6974	9124.39	134105	3384.36
50	180.433	25.003	9.92203	16641.2	12.7129	13152.2	167204	3354.4
62.9463	191.297	25.001	9.89894	20656	11.0712	18771.5	207822	3315.03
79.2447	198.195	25.002	9.8636	25554.2	9.70742	26548	257712	3269.32
100	203.558	25	9.80979	31444.6	8.55628	37209.6	318376	3213.04

Table 7M

Summary of Complex Viscosity Results for Example 16

Example 16					
Angular frequency (rad/s)	Complex viscosity (Pa.s)				
	50%	70%	80%	90%	100%
0.5	0.105533	7.47092	13.5757	83.9123	5646.72
0.629463	0.122633	7.93567	13.927	84.1518	5646.29

0.792447	0.129495	7.52153	13.8261	84.3409	5637.15
0.997631	0.191276	7.75737	13.5734	84.8484	5641.97
1.25594	0.191112	7.40771	13.7863	84.5137	5642.45
1.58114	0.129922	7.52854	13.7676	84.7718	5644.34
1.99054	0.337734	7.58655	13.9726	84.9731	5640.28
2.50594	0.216909	7.65407	13.6761	84.9718	5637.92
3.15479	0.269861	7.51068	13.8431	84.9111	5639.42
3.97164	0.093719	7.42453	13.7181	84.8793	5633.66
5	0.209489	7.38394	13.6169	84.8166	5622.26
6.29463	0.222806	7.49509	13.7072	84.824	5617.06
7.92447	0.234527	7.48388	13.6772	84.9318	5607.96
9.97631	0.185656	7.4701	13.6809	84.9645	5593.12
12.5594	0.224774	7.47754	13.6334	84.8985	5574.59
15.8114	0.192582	7.44458	13.6438	84.9253	5550.53
19.9054	0.187578	7.45628	13.6316	84.8738	5516.93
25.0594	0.184162	7.43339	13.6288	84.8415	5472.77
31.5479	0.200011	7.43298	13.623	84.8293	5417.6
39.7164	0.200585	7.43123	13.6142	84.7666	5347.32
50	0.199106	7.42689	13.6037	84.7183	5261.29
62.9463	0.195072	7.42745	13.6023	84.6411	5153.66
79.2447	0.193491	7.41988	13.5977	84.5397	5022.96
100	0.18912	7.42501	13.5857	84.4486	4888.67

Table 7N

Complex Viscosity Results for Example 16 at 50% Polymer Content

Example 16 (50% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1403	25.118	9.96561	5.26E-03	0.886944	0.039476	0.035013	0.105533
0.629463	45.1452	25.122	9.96192	7.69E-03	1.85388	-0.03665	-0.06794	0.122633
0.792447	61.0347	25.105	9.95764	0.010218	1.04065	0.071102	0.073992	0.129495
0.997631	73.6638	25.077	9.95717	0.019001	-2.93439	-0.06155	0.180622	0.191276
1.25594	83.7082	25.048	9.96053	0.023908	-6.63445	-0.03577	0.237344	0.191112
1.58114	91.6922	25.034	9.95841	0.020457	-7.77534	-0.0262	0.203746	0.129922
1.99054	98.041	25.017	9.95582	0.06693	2.00047	0.300593	0.601327	0.337734
2.50594	103.086	25.009	9.96033	0.05414	3.31513	0.156977	0.5204	0.216909
3.15479	107.098	25.003	9.95661	0.084766	1.63475	0.444257	0.72625	0.269861
3.97164	110.3	24.989	9.95663	0.03706	1.65976	0.192089	0.318823	0.093719

5	112.844	24.993	9.96171	0.104343	-10.1032	-0.10317	1.04235	0.209489
6.29463	121.891	24.979	9.95599	0.13963	49.2616	0.028464	1.40219	0.222806
7.92447	129.094	24.975	9.95655	0.185042	4.39712	0.412141	1.81223	0.234527
9.97631	136.069	24.964	9.95749	0.184426	-26.0577	-0.07103	1.8508	0.185656
12.5594	142.623	24.961	9.95853	0.281127	196.805	0.014344	2.82299	0.224774
15.8114	149.892	24.964	9.95487	0.303114	11.7611	0.257972	3.03404	0.192582
19.9054	160.054	24.96	9.95388	0.371636	14.4701	0.257423	3.72493	0.187578
25.0594	165.401	24.965	9.95027	0.459157	11.9189	0.385843	4.59883	0.184162
31.5479	172.98	24.971	9.94365	0.627352	83.3406	0.075707	6.30948	0.200011
39.7164	179.558	24.974	9.93387	0.791215	19.9635	0.398554	7.95655	0.200585
50	184.969	24.976	9.91849	0.987074	41.7568	0.238343	9.95244	0.199106
62.9463	192.944	24.98	9.89381	1.21418	18.5054	0.662572	12.2612	0.195072
79.2447	199.753	24.99	9.85841	1.51021	94.6828	0.161933	15.3322	0.193491
100	205.792	24.989	9.804	1.8513	22.8175	0.828041	18.8939	0.18912

Table 70
Complex Viscosity Results for Example 16 at 70% Polymer Content

Example 16 (70% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	25.021	9.96147	0.372106	74.6941	0.050006	3.73512	7.47092
0.629463	45.1433	24.978	9.96053	0.497549	69.6255	0.071737	4.99469	7.93567
0.792447	61.033	24.958	9.95743	0.593504	39.4961	0.150863	5.9585	7.52153
0.997631	73.6622	24.958	9.95787	0.770639	-37.0639	-0.20873	7.73618	7.75737
1.25594	83.7068	24.95	9.9614	0.926775	-41.2524	-0.22546	9.30093	7.40771
1.58114	91.6905	24.956	9.95901	1.18549	37.8149	0.314678	11.8995	7.52854
1.99054	98.0395	24.958	9.9563	1.50353	-47.9879	-0.31462	15.098	7.58655
2.50594	103.085	24.961	9.96071	1.91052	95.0994	0.201679	19.1795	7.65407
3.15479	107.097	24.965	9.95698	2.35927	141.207	0.167797	23.694	7.51068
3.97164	110.298	24.973	9.95701	2.93608	-258.528	-0.11406	29.4874	7.42453
5	114.099	24.979	9.9619	3.6779	-440.893	-0.08374	36.9196	7.38394
6.29463	123.149	24.981	9.95646	4.69734	277.137	0.170235	47.1785	7.49509
7.92447	130.345	24.983	9.95698	5.90506	463.186	0.128038	59.3056	7.48388
9.97631	136.055	24.989	9.95781	7.42096	162.588	0.458353	74.5226	7.4701
12.5594	141.112	25	9.95868	9.35257	156.075	0.60171	93.9118	7.47754
15.8114	148.783	25	9.95533	11.7183	214.669	0.548322	117.708	7.44458
19.9054	155.154	25.003	9.95413	14.7739	150.952	0.983207	148.417	7.45628
25.0594	160.5	25.007	9.95052	18.5354	169.552	1.09863	186.273	7.43339
31.5479	171.066	25.01	9.94402	23.3182	171.563	1.36679	234.491	7.43298

39.7164	177.639	25.015	9.93446	29.3207	176.93	1.6681	295.137	7.43123
50	183.055	25.015	9.91906	36.8339	154.585	2.40215	371.337	7.42689
62.9463	190.922	25.011	9.89504	46.2623	169.162	2.76375	467.522	7.42745
79.2447	197.816	25.013	9.85971	57.9737	228.088	2.57786	587.98	7.41988
100	203.163	25.014	9.80531	72.8045	258.415	2.87327	742.496	7.42501

Table 7P
Complex Viscosity Results for Example 16 at 80% Polymer Content

Example 16 (80% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1403	25.066	9.96234	0.676228	58.8906	0.115246	6.78686	13.5757
0.629463	45.1432	25.027	9.96037	0.873182	51.0661	0.171638	8.76488	13.927
0.792447	61.0328	24.999	9.95754	1.09099	-209.476	-0.0523	10.9563	13.8261
0.997631	73.662	24.98	9.95749	1.34837	150.976	0.089689	13.541	13.5734
1.25594	83.7065	24.975	9.96108	1.72474	202.555	0.085481	17.3146	13.7863
1.58114	91.6883	24.972	9.95854	2.16783	92.5842	0.235108	21.7673	13.7676
1.99054	98.0362	24.965	9.9563	2.76913	57.9032	0.480263	27.8088	13.9726
2.50594	105.591	24.965	9.96028	3.41353	-17810.5	-1.93E-03	34.2714	13.6761
3.15479	109.602	24.965	9.95702	4.34845	125.891	0.346894	43.6708	13.8431
3.97164	112.803	24.963	9.95691	5.42488	215.507	0.252812	54.483	13.7181
5	115.346	24.968	9.96182	6.78246	278.907	0.244109	68.0841	13.6169
6.29463	124.393	24.972	9.95665	8.59074	169.699	0.508429	86.28	13.7072
7.92447	131.587	24.975	9.95663	10.7914	172.239	0.629255	108.382	13.6772
9.97631	137.295	24.978	9.9578	13.5909	169.23	0.806489	136.482	13.6809
12.5594	142.35	24.98	9.95862	17.052	168.459	1.01642	171.225	13.6334
15.8114	150.02	24.983	9.95542	21.4765	163.351	1.32061	215.723	13.6438
19.9054	156.392	24.987	9.95433	27.0103	166.496	1.6297	271.338	13.6316
25.0594	161.737	24.985	9.95079	33.985	161.08	2.12021	341.524	13.6288
31.5479	169.315	24.999	9.94451	42.739	185.228	2.32022	429.769	13.623
39.7164	175.726	24.997	9.93514	53.72	163.411	3.3088	540.697	13.6142
50	181.14	25	9.91983	67.4732	169.593	4.01062	680.173	13.6037
62.9463	190.503	25.003	9.89617	84.7325	169.816	5.04193	856.201	13.6023
79.2447	197.315	25.007	9.86085	106.255	184.098	5.85302	1077.53	13.5977
100	202.663	25.01	9.80681	133.233	155.467	8.73847	1358.55	13.5857

Table 7Q
Complex Viscosity Results for Example 16 at 90% Polymer Content

Example 16 (90% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	25.065	9.96435	4.18066	167.363	0.250685	41.9554	83.9123
0.629463	45.1452	25.066	9.96133	5.27656	182.44	0.290338	52.9696	84.1518
0.792447	61.035	25.058	9.95806	6.65553	109.399	0.610907	66.8329	84.3409
0.997631	73.6643	25.037	9.95713	8.42845	76.8358	1.10157	84.6403	84.8484
1.25594	83.7065	25.023	9.96129	10.5734	127.37	0.833327	106.141	84.5137
1.58114	91.6885	25.011	9.95834	13.3478	84.3812	1.58835	134.027	84.7718
1.99054	98.0362	25.003	9.95631	16.8403	101.728	1.66261	169.134	84.9731
2.50594	103.084	25.004	9.96022	21.2087	98.2542	2.16706	212.923	84.9718
3.15479	107.097	25	9.95709	26.6727	93.7945	2.85583	267.861	84.9111
3.97164	110.298	24.992	9.95655	33.5645	150.884	2.23419	337.103	84.8793
5	112.843	24.989	9.96217	42.2479	132.853	3.19202	424.071	84.8166
6.29463	121.89	24.983	9.95656	53.1616	146.84	3.63609	533.923	84.824
7.92447	129.093	24.981	9.95689	67.0138	141.062	4.77112	673.022	84.9318
9.97631	134.809	24.976	9.95823	84.4093	138.756	6.10863	847.611	84.9645
12.5594	139.871	24.977	9.95935	106.194	149.475	7.13332	1066.25	84.8985
15.8114	147.546	24.976	9.95673	133.698	152.284	8.81748	1342.76	84.9253
19.9054	153.92	24.976	9.95615	168.204	144.937	11.6561	1689.4	84.8738
25.0594	159.269	24.978	9.95378	211.625	138.062	15.399	2126.02	84.8415
31.5479	166.85	24.981	9.94884	266.249	127.764	20.9456	2676.1	84.8293
39.7164	173.261	24.981	9.94215	334.715	119.854	28.0884	3366.51	84.7666
50	178.676	24.983	9.9283	420.555	111.212	38.087	4235.74	84.7183
62.9463	186.544	24.985	9.90649	527.803	102.997	51.7257	5327.59	84.6411
79.2447	193.437	24.992	9.87429	661.51	95.586	70.083	6698.95	84.5397
100	198.784	24.99	9.82073	829.346	86.9278	97.1416	8444.3	84.4486

Complex Viscosity Results for Example 16 at 100% Polymer Content

Example 16 (100% polymer content)								
Angular frequency (rad/s)	Step time (s)	Temp. (°C)	Oscillation strain (%)	Oscillation stress (Pa)	Tan(delta)	Storage modulus (Pa)	Loss modulus (Pa)	Complex viscosity (Pa.s)
0.5	25.1405	24.999	9.96334	281.301	127.034	22.2244	2823.27	5646.72
0.629463	45.1492	24.994	9.96165	354.05	169.254	20.9984	3554.07	5646.29
0.792447	61.0428	24.999	9.95799	444.838	146.527	30.4861	4467.04	5637.15

0.997631	73.6758	24.997	9.95802	560.498	126.418	44.5223	5628.43	5641.97
1.25594	83.7225	24.997	9.96153	705.934	140.443	50.4576	7086.42	5642.45
1.58114	91.7083	24.997	9.95882	888.773	106.399	83.8737	8924.09	5644.34
1.99054	98.0568	25.002	9.95598	1117.78	88.3861	127.016	11226.5	5640.28
2.50594	103.104	25	9.96055	1407.25	79.0064	178.81	14127.1	5637.92
3.15479	107.119	24.999	9.95686	1771.44	65.0291	273.556	17789.1	5639.42
3.97164	110.313	24.999	9.9571	2227.89	54.8691	407.718	22371.2	5633.66
5	112.862	25.001	9.96187	2800.41	44.9282	625.539	28104.3	5622.26
6.29463	121.915	25	9.95669	3520.41	37.5097	942.283	35344.7	5617.06
7.92447	129.112	25	9.95699	4424.89	30.878	1438.46	44416.8	5607.96
9.97631	134.824	24.996	9.95814	5556.51	25.7789	2162.88	55756.7	5593.12
12.5594	139.884	25.004	9.95903	6972.69	21.3683	3272.94	69937.2	5574.59
15.8114	147.558	24.999	9.95621	8737.73	17.8235	4916.18	87623.8	5550.53
19.9054	153.932	24.997	9.95533	10932.6	14.9148	7346.43	109570	5516.93
25.0594	159.282	25	9.95248	13649.2	12.5399	10902	136710	5472.77
31.5479	166.864	24.999	9.94713	17001	10.6275	16011.4	170162	5417.6
39.7164	173.436	25	9.93827	21106.5	9.09276	23216.7	211103	5347.32
50	179.983	24.997	9.92389	26106.2	7.86309	33188.3	260962	5261.29
62.9463	187.85	25.004	9.90114	32119.6	6.87049	46724.6	321021	5153.66
79.2447	194.745	25.001	9.86524	39267.9	6.07475	64653.9	392757	5022.96
100	200.105	25.003	9.81108	47849.5	5.46566	87774.5	479745	4888.67

APPENDIX B**Table 9**

Comparison of 1st order monomer conversion viscosities over time for poly(propylene fumarate-co-succinate) copolymers made with different orders of addition for the reactive species

Catalyst + alcohol		Catalyst + Maleic anhydrid	
Time (hrs)	$\ln([M_0/M_t])$	Time (hrs)	$\ln([M_0/M_t])$
2	0.1246	1.7	0.104
4	0.178	2.5	0.113
6	0.246	4	0.1658
8	0.321	5	0.24
10.1	0.372	6	0.5422
12	0.418	10	0.93
14	0.4589	14	1.21
16	0.5516	18	1.52
18	0.5979	22	1.756
20	0.6503	24	1.793
22	0.7181	26	1.825
24	0.7853	30	1.94
26.4	0.8542	50	2.01
41	1.44		
44.5	1.78		
48	2.08		
50	2.10		
52	2.23		

Table 10

Comparison of MAn conversion percentage over time for poly(propylene fumarate-co-succinate) copolymers made with different orders of addition for the reactive species

Catalyst + alcohol		Catalyst + Maleic anhydride	
Time (hrs)	MAn conversion (%)	Time (hrs)	MAn conversion (%)
2	11.7	1.7	10
4	16.3	2.5	11
6	21.8	4	15.28
8	27.5	5	21.32
10.1	31.05	6	41.85
12	34.16	10	60.5

14	36.8	14	70.15
16	40.28	18	78.11
18	43.97	22	82.72
20	48.11	24	83.35
22	51.28	26	83.98
24	54.41	30	85.5
26.4	57.76	50	86.7
41	76.3	50	86.7
44.5	83.2		
48	87.6		
50	89.5		
52	93		

Table 11

Comparison of Mn and Đm at different MAn Conversion (%) for poly(propylene fumarate-co-succinate) copolymers made with different orders of addition for the reactive species

Catalyst + Maleic anhydride			Catalyst + alcohol		
MAn Conversion (%)	Mn (g.mol ⁻¹)	Đ _m	MAn Conversion (%)	Mn (g.mol ⁻¹)	Đ _m
10	337	-	21.8	504	-
11	393	-	27.5	622	-
15.28	477	-	31.05	713	-
21.32	555	-	34.16	824	-
41.85	1129	-	36.8	925	-
58.2	1769	2.05	40.28	1022	1.26
70.15	2022	1.93	43.97	1100	1.27
78.11	2382	1.7	48.11	1196	1.26
82.72	2549	1.57	51.28	1267	1.29
83.35	2610	1.53	54.41	1402	1.27
83.88	2628	1.52	57.76	1485	1.26
85.5	2761	1.48	76.3	2230	-
86.7	2836	1.48	83.2	2620	-
			87.6	2930	-
			86.4	2850	-

Table 12
Complex Viscosity for Clear PPF/DEF with 50% Polymer Content

Clear PPF/DEF 50 % polymer content								
Angular frequency	Step time	Temp.	Oscillation strain	Oscillation stress	Tan (delta)	Storage modulus	Loss modulus	Complex viscosity
rad/s	s	°C	%	Pa		Pa	Pa	Pa.s
0.628319	20.0053	24.999	4.98085	0.016501	11.6995	0.028214	0.330092	0.527273
0.995818	32.6945	25.004	4.97983	0.024773	4.35955	0.111219	0.484866	0.499547
1.57826	40.7153	25	4.9798	0.039194	11.6734	0.067177	0.784177	0.49868
2.50138	45.8047	25.003	4.98102	0.062835	40.377	0.031233	1.26111	0.504319
3.96442	50.6218	24.999	4.97574	0.099409	70.3467	0.028398	1.99767	0.50395
6.28319	59.7183	25.002	4.97921	0.153472	38.44	0.080157	3.08122	0.490557
9.95818	65.4897	25.007	4.97968	0.244125	34.3133	0.142812	4.90034	0.492301
15.7826	72.8132	25.007	4.97902	0.385825	141.672	0.054696	7.74881	0.490983
25.0138	78.2372	25.002	4.9752	0.609929	93.869	0.130593	12.2587	0.490104
39.6442	84.4727	25.001	4.96907	0.966296	95.0724	0.20453	19.4452	0.490519
62.8319	95.451	25.001	4.94869	1.52735	166.334	0.185548	30.8631	0.49121
99.5818	101.373	25.003	4.90653	2.3994	117.908	0.414734	48.9004	0.491076
157.826	107.749	25.007	4.8164	3.72616	411.455	0.188025	77.3639	0.490185
250.138	115.877	24.997	4.67194	5.71663	-663.478	-0.18442	122.361	0.489176
396.442	121.947	25.005	4.48925	8.75216	-41.981	-4.6427	194.905	0.491775
628.319	129.027	25.001	4.25825	13.1973	-197.153	-1.57201	309.928	0.493272

Table 13
Complex Viscosity for Dark PPF/DEF with 60% Polymer Content

Clear PPF/DEF 60 % polymer content								
Angular frequency	Step time	Temp.	Oscillation strain	Oscillation stress	Tan (delta)	Storage modulus	Loss modulus	Complex viscosity
rad/s	s	°C	%	Pa		Pa	Pa	Pa.s
0.628319	20.0053	24.995	4.98229	0.051414	14.2267	0.072356	1.02938	1.64236
0.995818	32.6945	24.997	4.97935	0.079126	28.6516	0.055428	1.58811	1.59575
1.57826	40.7155	24.997	4.98061	0.125058	43.9614	0.057101	2.51025	1.59093
2.50138	45.8045	24.997	4.98035	0.204265	36.5354	0.112217	4.09989	1.63966
3.96442	49.0355	24.994	4.97692	0.320454	67.8929	0.094827	6.43809	1.62414
6.28319	59.1335	24.997	4.9781	0.50391	66.236	0.152808	10.1214	1.61105
9.95818	64.8943	25	4.98044	0.79471	73.9413	0.215781	15.9551	1.60236
15.7826	72.2143	25.001	4.9802	1.25838	75.8813	0.332959	25.2654	1.60097
25.0138	77.635	25	4.97778	1.98942	81.5641	0.489958	39.963	1.59776

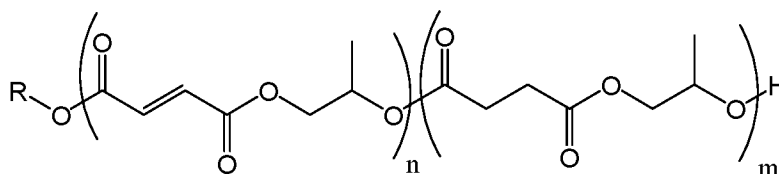
39.6442	83.8688	25.001	4.97437	3.14841	85.4593	0.740566	63.2883	1.59652
62.8319	91.8497	24.999	4.95779	4.97329	93.4413	1.07348	100.307	1.59653
99.5818	97.7658	25	4.91667	7.797	112.104	1.41455	158.577	1.59249
157.826	104.139	24.999	4.82572	12.1184	144.294	1.74031	251.116	1.59113
250.138	116.64	24.997	4.66541	18.5841	300.724	1.32459	398.335	1.59247
396.442	122.711	25	4.43794	28.2372	-97.4327	-6.52998	636.234	1.60494
628.319	129.804	24.998	4.10345	42.9125	-93.5594	-11.1769	1045.71	1.66439

CLAIMS

What is claimed is:

1. A polymer composition comprising the one or more isomerized residues of maleic anhydride monomer, one or more residue of succinic anhydride monomer and one or more residues of propylene oxide monomer.
2. The polymer composition of claim 1 comprising from about 1 to about 30 mole percent, preferably from about 1 to about 20 mole percent, and more preferably from about 1 to about 10 mole percent succinic anhydride residues.
3. The polymer composition of claim 1 comprising about 50 mole percent propylene oxide residues.
4. The polymer composition of claim 1 having a degree of polymerization (DP) of from about 5 to about 100, preferably from about 5 to about 50, and more preferably from about 5 to about 10.
5. The polymer composition of claim 1 having a number average molecular weight (M_n) of from about 0.5 kDa to about 100 kDa, preferably from about 0.5 kDa to about 50 kDa, and more preferably from about 0.5 kDa to about 5 kDa, as measured by size exclusion chromatography (SEC) or gel permeation chromatography (GPC).
6. The polymer composition of claim 1 having a mass distribution ($\mathcal{D}_m$) of from about 1 to about 2, preferably from about 1 to about 1.5, and more preferably from about 1 to about 1.2.
7. The polymer composition of claim 1 having a zero sheer viscosity of from about 500 Pa·s to about 10,000 Pa·s, preferably from about 1000 Pa·s to about 7,000 Pa·s, and more preferably from about 1000 Pa·s to about 5000 Pa·s, as measured by a rheometer.

8. The polymer composition of claim 1 having a zero shear viscosity of from about 1.5 Pa·s to about 2.5 Pa·s, preferably from about 1.7 Pa·s to about 2.4 Pa·s, and more preferably from about 1.8 Pa·s to about 2.2 Pa·s, as measured by a rheometer when diluted with 30 weight percent DEF.
9. The polymer composition of claim 1 having an absorbance at wavelengths from about 305 nm to about 405 nm of from about 0.001 to about 0.3, preferably from about 0.001 to about 0.2, and more preferably from about 0.001 to about 0.1, as measured by a UV-Visible spectrometer.
10. The polymer composition of claim 1 having the formula:

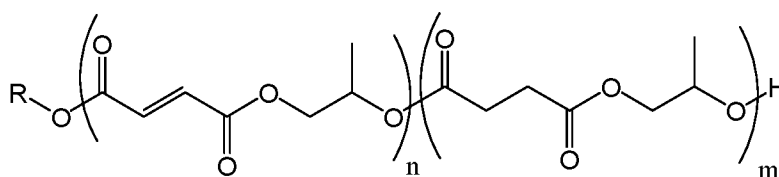


where R is alkyl, alkene, alkyne or aromatic group; n is a mole fraction from about 0.50 to about 0.99 and m is a mole fraction from about 0.01 to about 0.50.

11. A polymer for use in 3D printable resins comprising the isomerized reaction product of maleic anhydride, succinic anhydride and propylene oxide.
12. The polymer for use in 3D printable resins of claim 11 comprising from about 1 to about 30 mole percent, preferably from about 1 to about 20 mole percent, and more preferably from about 1 to about 10 mole percent succinic anhydride residues.
13. The polymer for use in 3D printable resins of claim 11 having a degree of polymerization (DP) of from about 5 to about 100, preferably from about 5 to about 50, and more preferably from about 5 to about 10.
14. The polymer for use in 3D printable resins of claim 11 having a number average molecular mass (M_n) of about 0.5 kDa to about 100 kDa, preferably from about 0.5 kDa to about 50 kDa, and more preferably from about 0.5 kDa to about 5 kDa, as

measured by size exclusion chromatography (SEC) or gel permeation chromatography (GPC).

15. The polymer for use in 3D printable resins of claim 11 having a mass distribution ($\mathcal{D}_m$) of from about 1 to about 2, preferably from about 1 to about 1.5, and more preferably from about 1 to about 1.2.
16. The polymer for use in 3D printable resins of claim 11 having a zero sheer viscosity of from about 500 Pa·s to about 10,000 Pa·s, preferably from about 1000 Pa·s to about 7,000 Pa·s, and more preferably from about 1000 Pa·s to about 5000 Pa·s, as measured by a rheometer.
17. The polymer for use in 3D printable resins of claim 11 having a zero sheer viscosity of from about 1.5 Pa·s to about 2.5 Pa·s, preferably from about 1.7 Pa·s to about 2.4 Pa·s, and more preferably from about 1.8 Pa·s to about 2.2 Pa·s, as measured by a rheometer when diluted with 30 weight percent DEF.
18. The polymer for use in 3D printable resins of claim 11 having an absorbance at wavelengths from about 305 nm to about 405 nm of from about 0.001 to about 0.3, preferably from about 0.001 to about 0.2, and more preferably from about 0.001 to about 0.1, as measured by a UV-Visible spectrometer.
19. The polymer for use in 3D printable resins of claim 11 having the formula:



where R is alkyl, alkene, alkyne or aromatic group; n is a mole fraction from about 0.50 to about 0.99 and m is a mole fraction from about 0.01 to about 0.50.

20. A method of making a polymer for use in 3D printable resins comprising:
 - A) reacting maleic anhydride, succinic anhydride and propylene oxide and an initiating alcohol in the presence of a magnesium catalyst to form a

poly(propylene maleate-co-succinate) copolymer intermediate having a maleic anhydride residue containing a *cis* double bond; and

- B) isomerizing the *cis* double bond in said maleic anhydride residue by reacting the poly(maleic anhydride-co-succinic anhydride-co-propylene oxide) polymer intermediate to form a poly(propylene fumarate-co-succinate) copolymer.

21. The method of claim 20 further comprising:

- C) washing the solution of step (B) with a buffer solution to remove any residual amine; and
D) drying the product of step (C) to recover the poly(propylene fumarate-co-succinate) copolymer.

22. The method of claim 20 wherein the initiating alcohol is selected from the group consisting of benzyl alcohol, propargyl alcohol, 4-hydroxybutan-2-one, 5-norbornen-2-ol, butanone, ethyl alcohol, isopropyl alcohol, tertiary butyl alcohol, and combinations thereof.

23. The method of claim 20 wherein the magnesium catalyst is $\text{Mg}(\text{BHT})_2(\text{THF})_2$.

24. The method of claim 20 wherein the step of reacting (step A) comprises:

- a) placing an initiating alcohol and $\text{Mg}(\text{BHT})_2(\text{THF})_2$ in a suitable sealed reaction vessel and then adding propylene oxide, maleic anhydride, succinic anhydride and a suitable solvent;
b) heating the combination of step (a) until substantially all of the maleic anhydride, succinic anhydride and propylene oxide have reacted to form a poly(propylene maleate-co-succinate) copolymer intermediate;
c) precipitating the poly(propylene maleate-co-succinate) copolymer intermediate into an excess of a non-solvent for said poly(propylene maleate-co-succinate) copolymer intermediate; and
d) drying the poly(propylene maleate-co-succinate) copolymer intermediate to remove remaining solvent.

25. The method of claim 24 wherein the suitable solvent in said step of combining (step a) is selected from toluene, hexane, and combinations thereof.
26. The method of claim 24 wherein the molar ratio of maleic anhydride to succinic anhydride in said step of combining (step a) is from about 100:1 to about 1:1, preferably from about 50:1 to about 1:1, and more preferably from about 2:1 to about 1:1.
27. The method of claim 24 wherein the step of heating (step b) comprises heating the combination of step (a) to a temperature of from about 40°C to about 80°C for from about 1 hours to about 48 hours or until substantially all of the maleic anhydride, succinic anhydride, and propylene oxide monomers have reacted.
28. The method of claim 24 wherein the step of precipitating (step c) comprises combining the product of step (b) with an excess of diethyl ether to cause the poly(propylene maleate-co-succinate) copolymer intermediate to precipitate out of solution.
29. The method of claim 24 wherein the step of drying (step d) is performed by vacuum evaporation.
30. The method of claim 20 wherein the step of isomerizing (step B) comprises:
1. dissolving the poly(propylene maleate-co-succinate) copolymer intermediate in a suitable solvent; and
 2. adding diethylamine to the solution of step (1) and heating it to a reflux temperature under an inert atmosphere to produce the poly(propylene fumarate-co-succinate) copolymer
31. The method of claim 30 wherein said suitable solvent for the poly(propylene maleate-co-succinate) copolymer intermediate in step (1) is selected from the group consisting of chloroform, dichloromethane, and combinations thereof.

32. The method of claim 30 wherein the solution of step (2) is heated to a reflux temperature under an inert atmosphere for from about 1 to about 48 hours or until substantially all of poly(propylene maleate-co-succinate) copolymer intermediate has isomerized.
33. The method of claim 30 wherein the buffer solution in said step of washing (step D) is a phosphate buffer solution.
34. The method of claim 30 wherein the step of drying (step D) is performed by vacuum evaporation.

Order of addition of reactive species

Order 1:

1. Maleic anhydride
2. Catalyst $\text{Mg}(\text{BHT})_2(\text{THF})_2$
3. Toluene
4. Initiator (Propargyl alcohol)
5. Propylene oxide

Order 2:

1. Initiator (Propargyl alcohol)
2. Catalyst $\text{Mg}(\text{BHT})_2(\text{THF})_2$
3. Toluene
4. Maleic anhydride
5. Propylene oxide

Polymers obtained

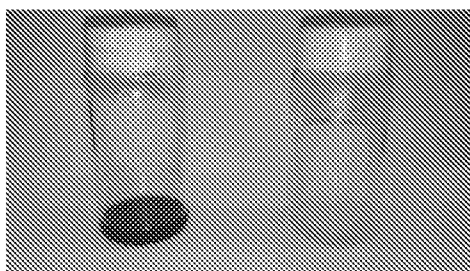


FIG. 1

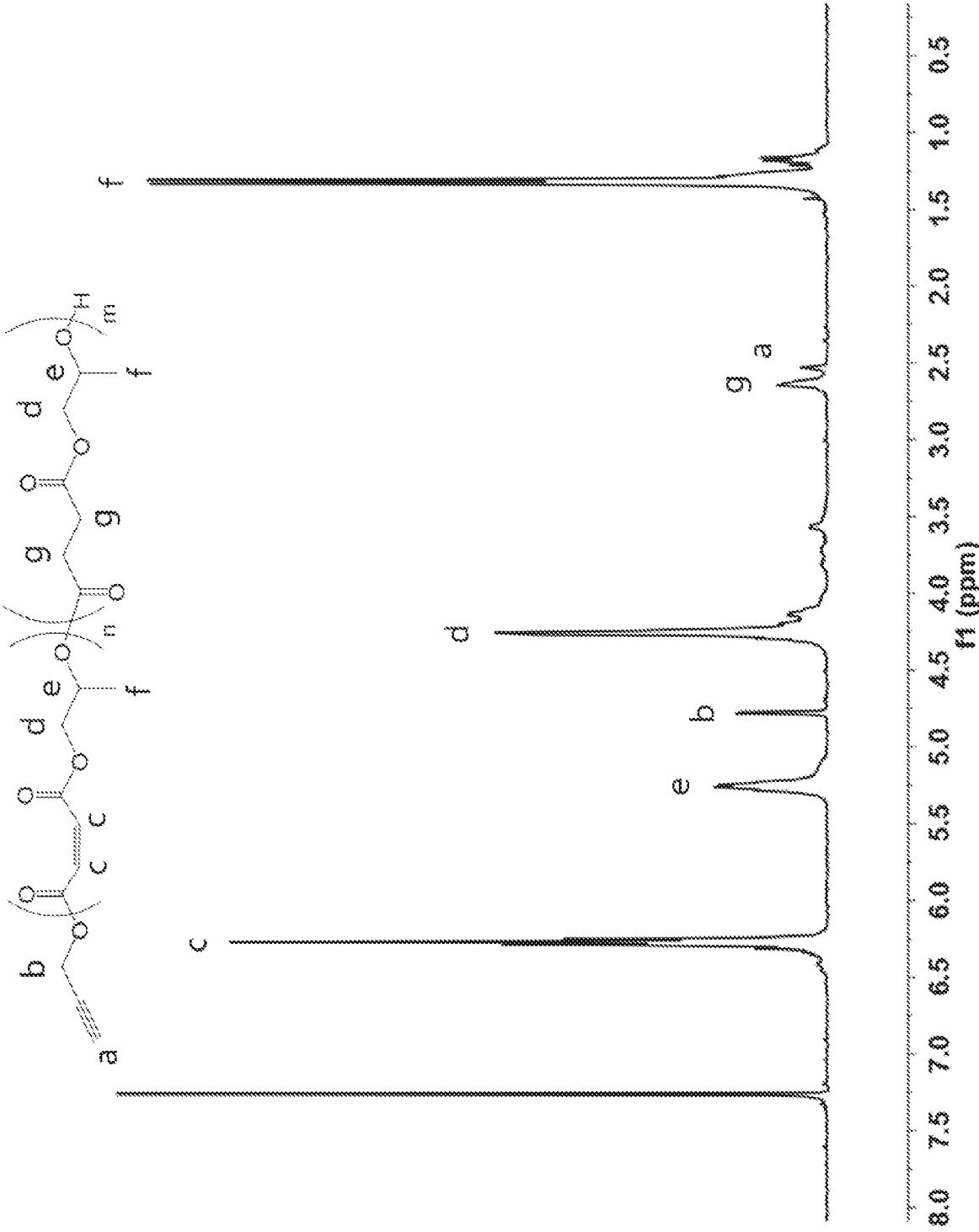


FIG. 2A

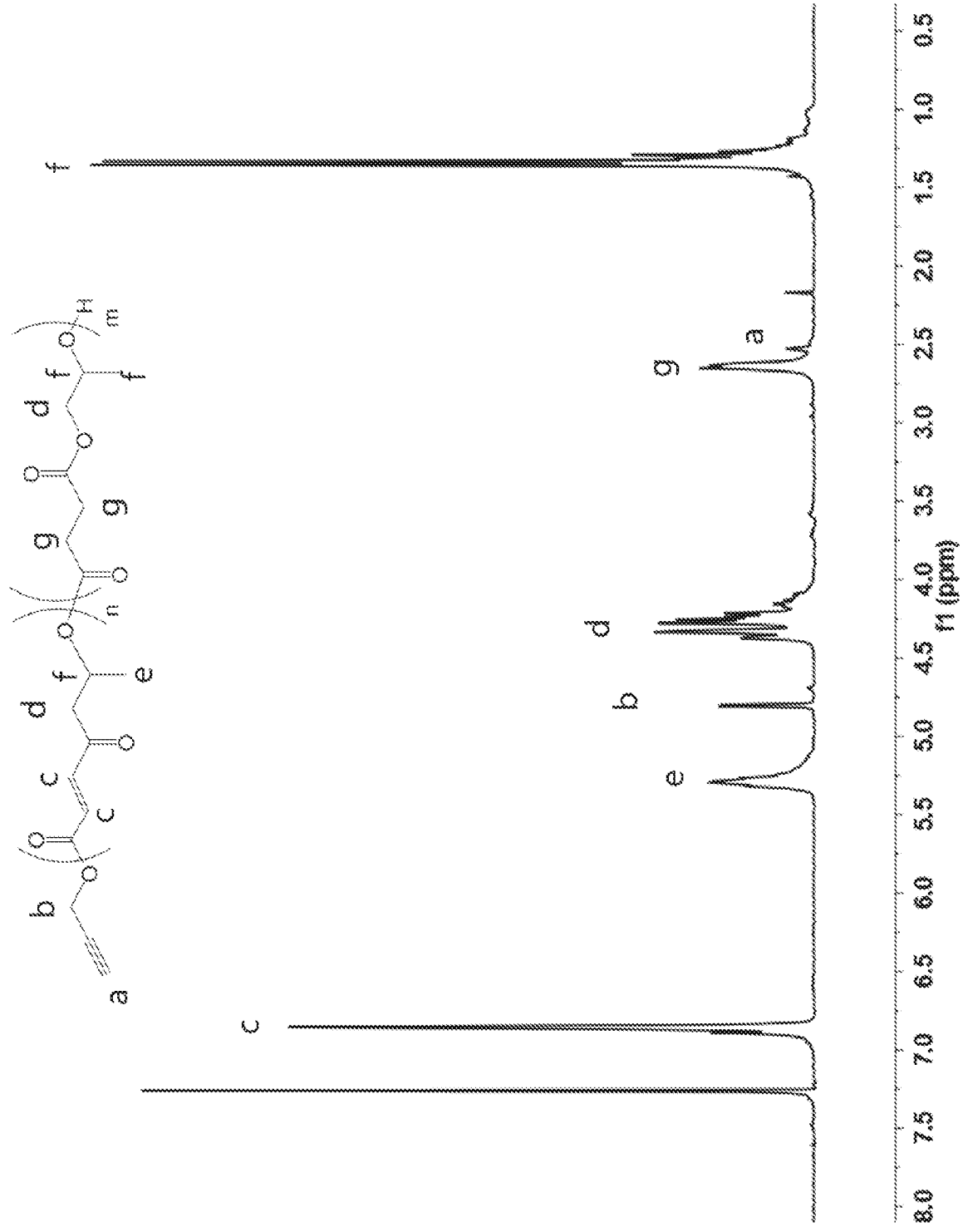
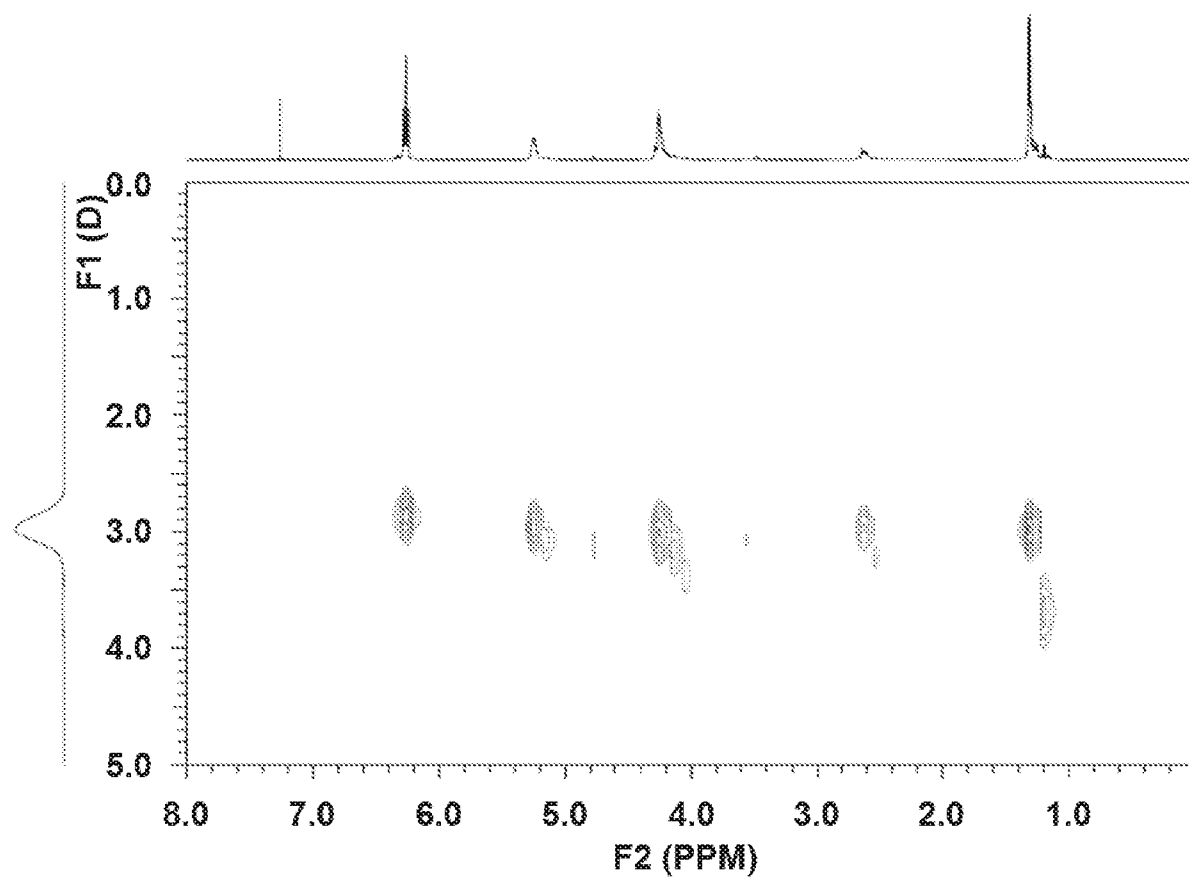
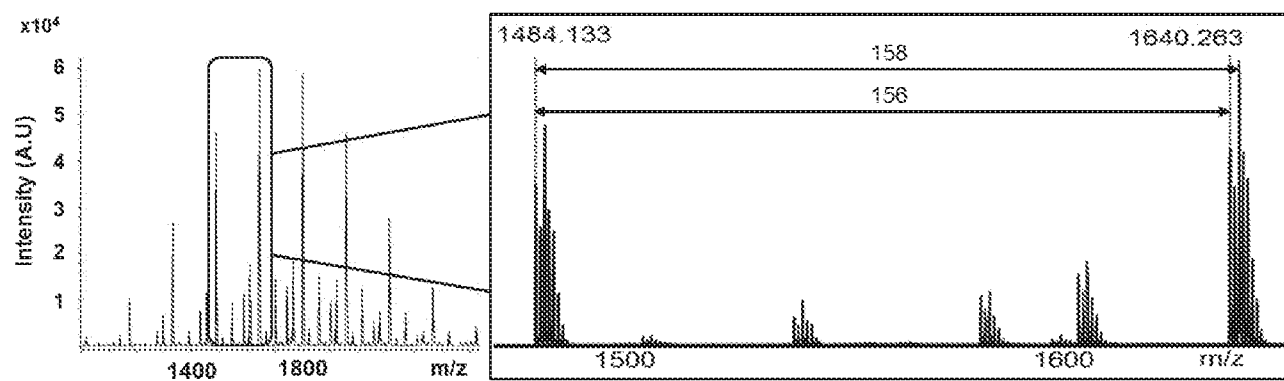
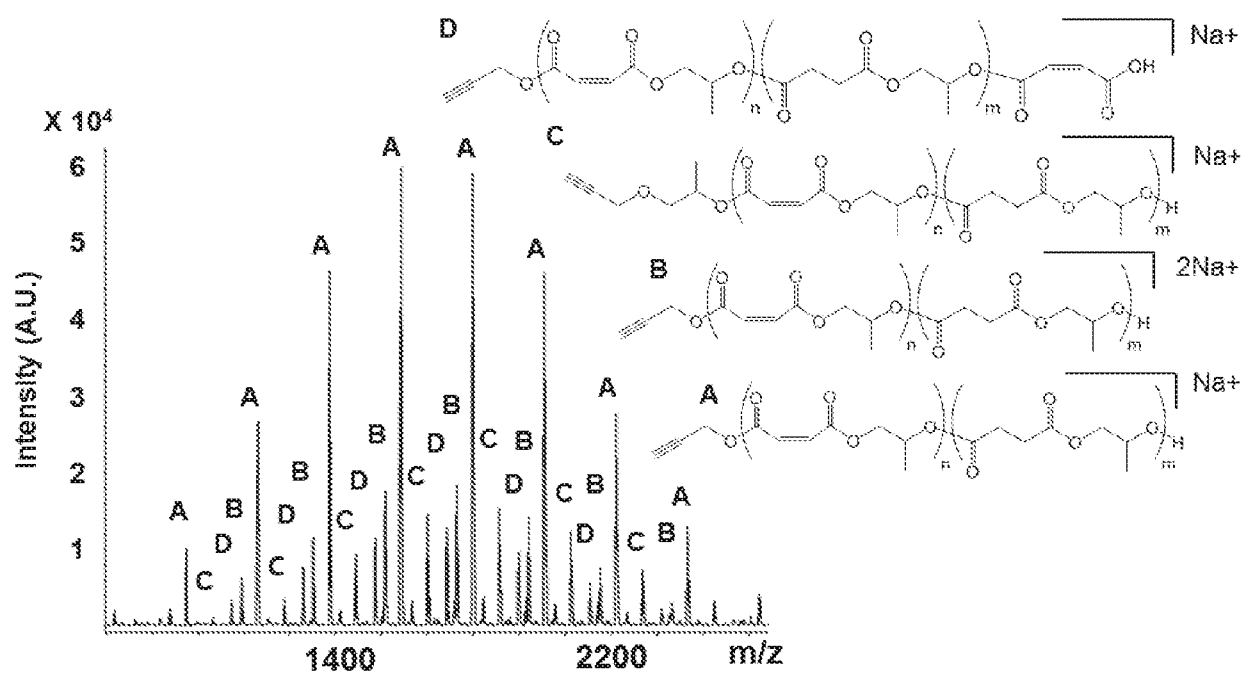
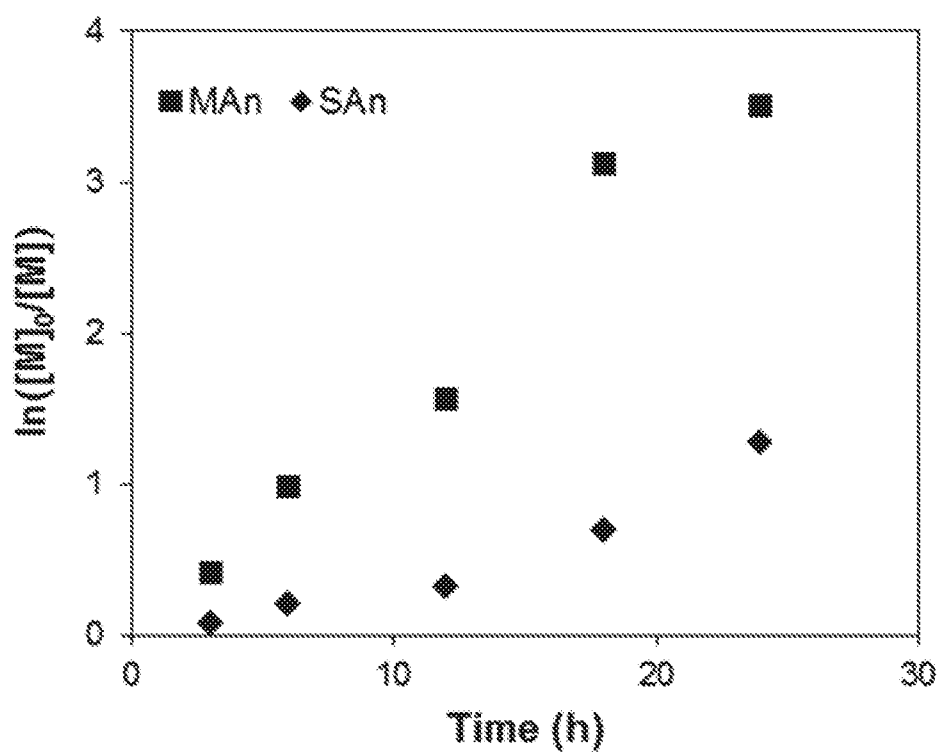
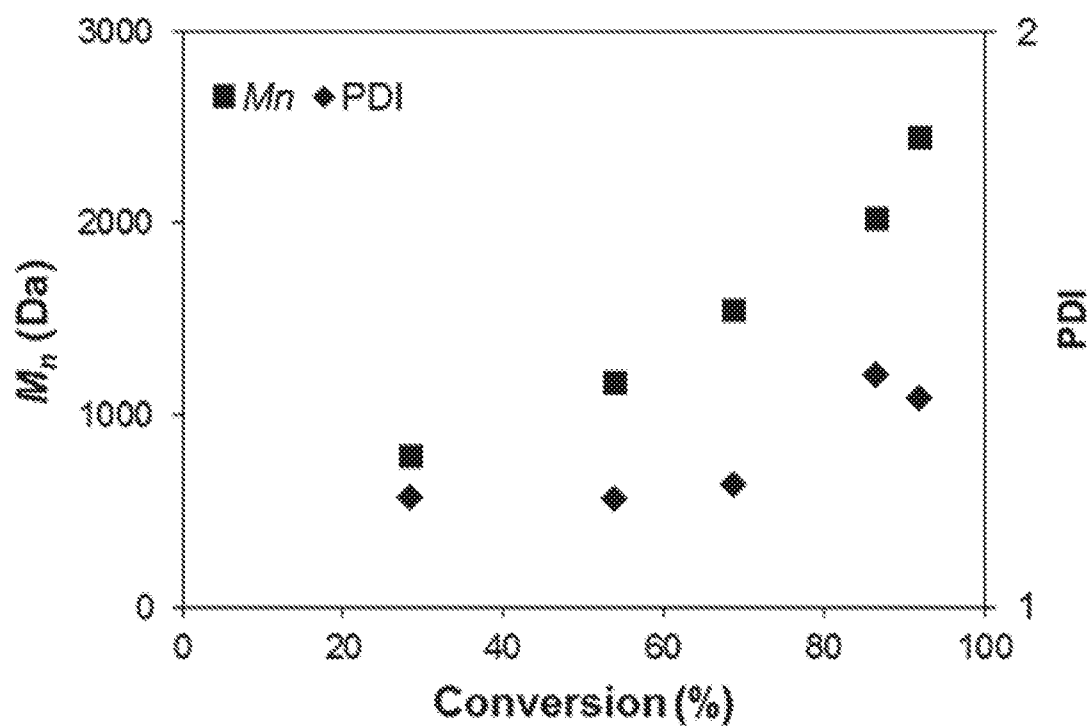
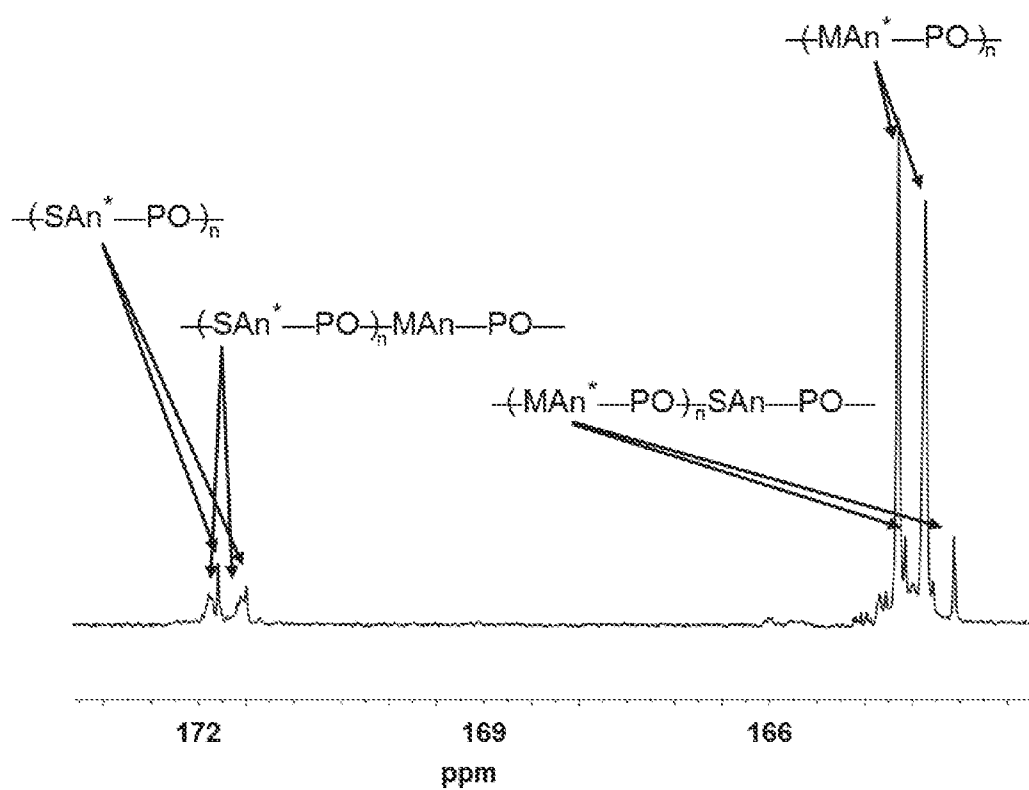


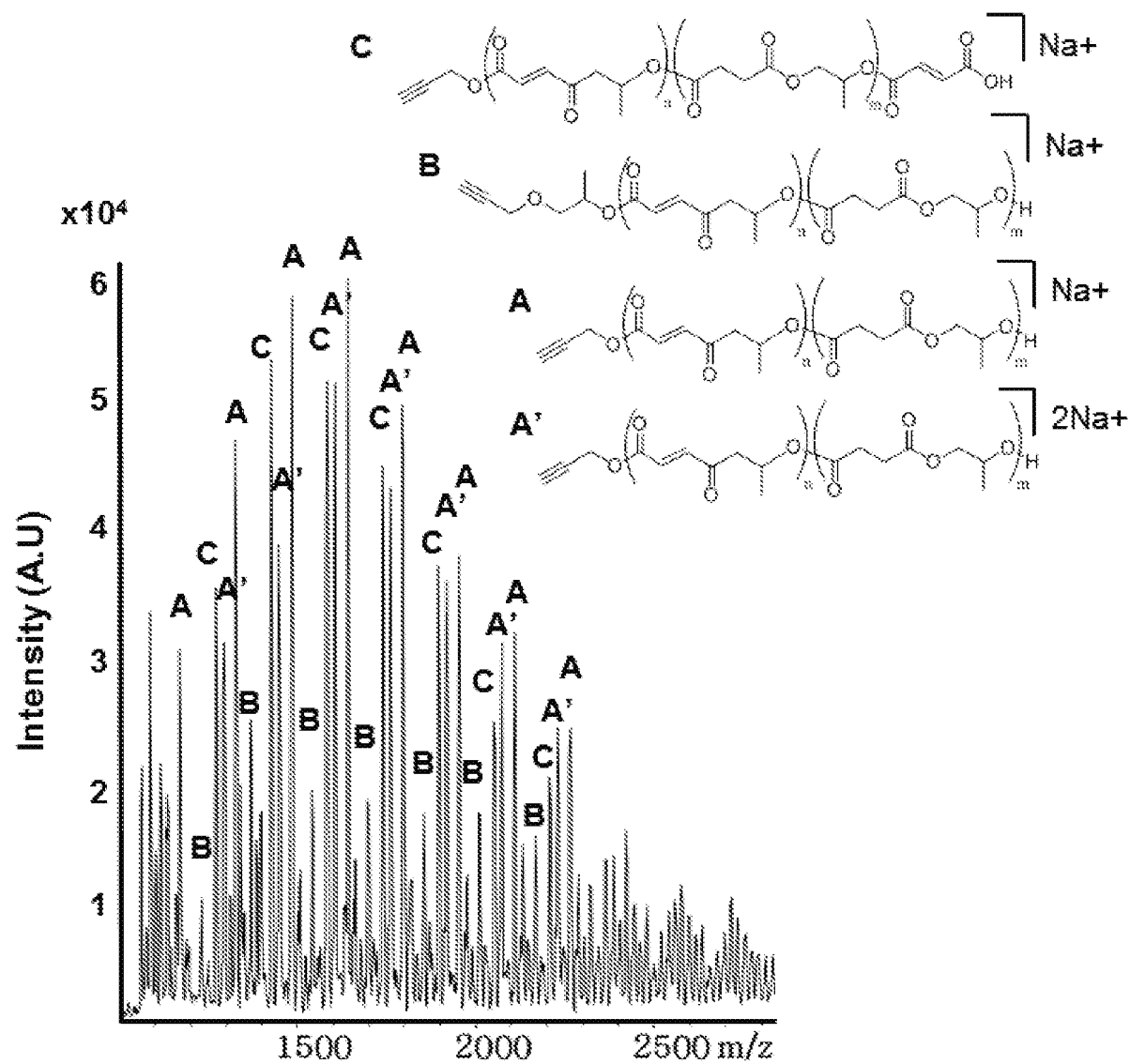
FIG. 2B

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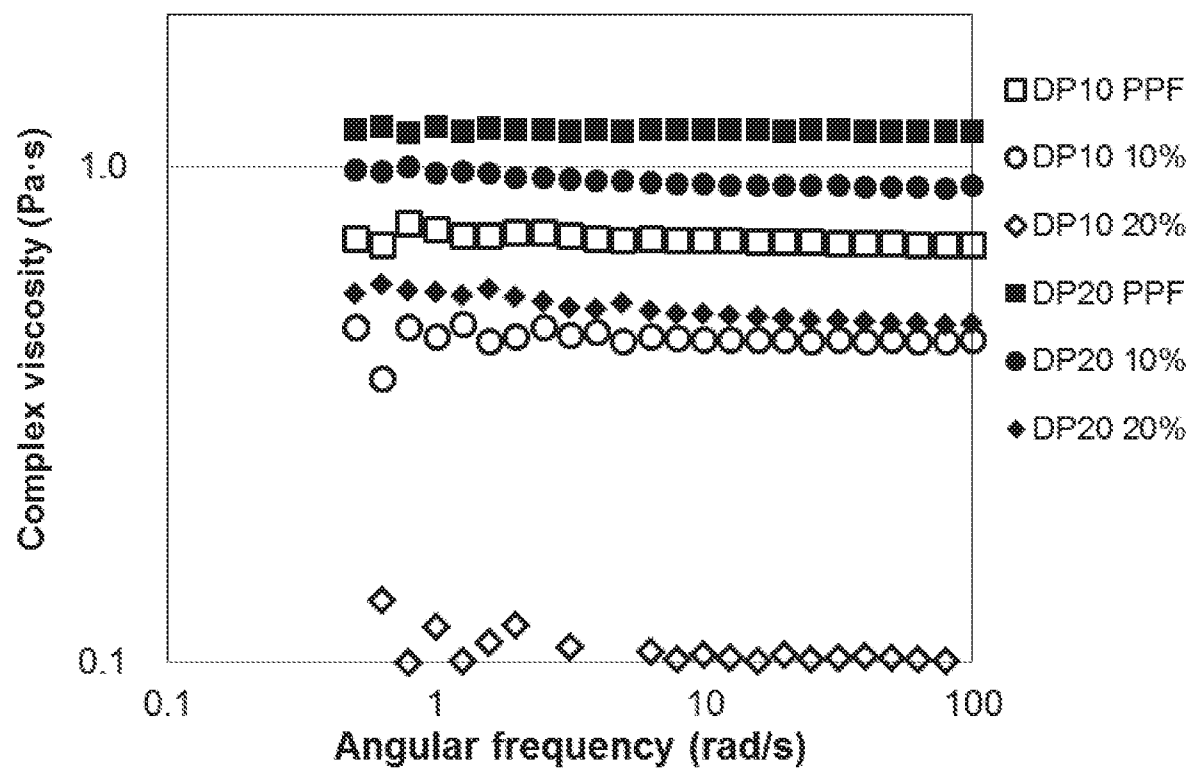
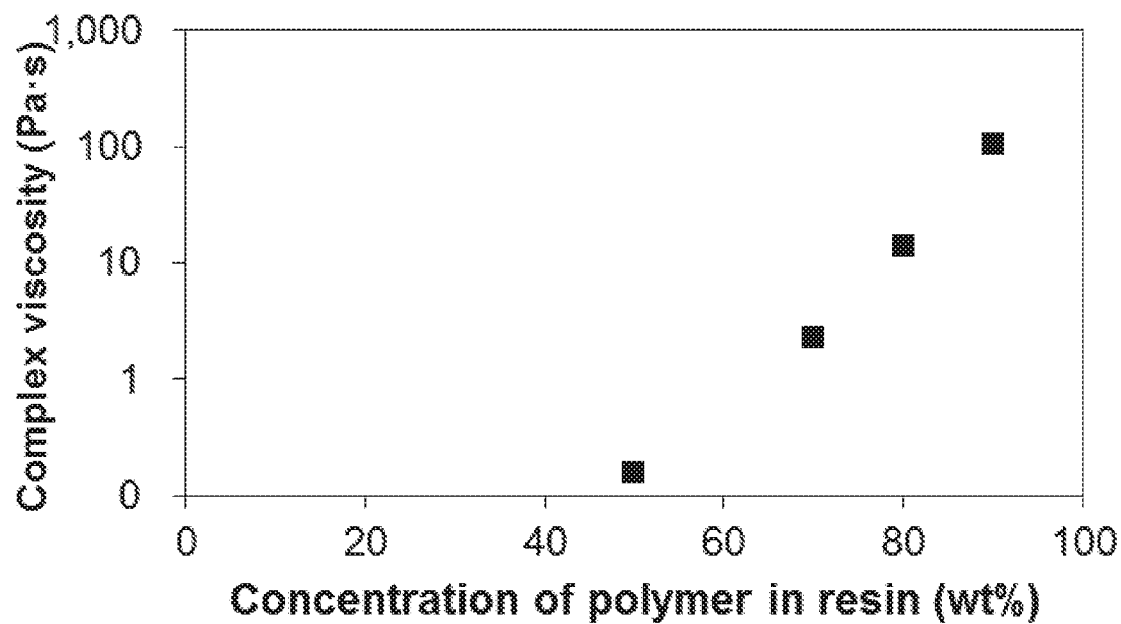
**FIG. 2C****FIG. 3**

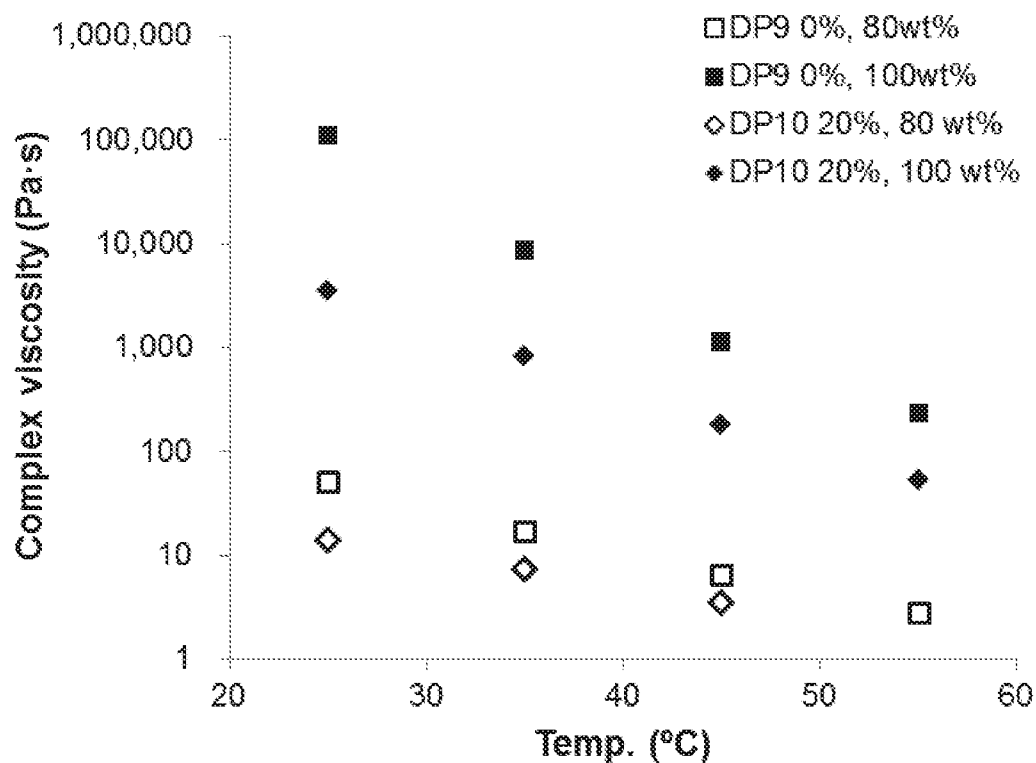
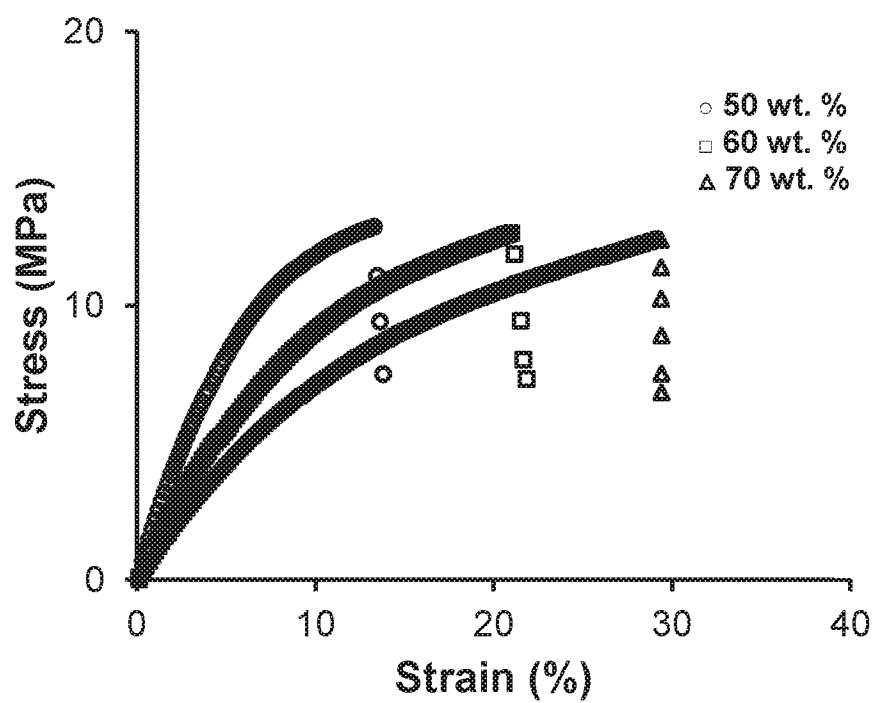
**FIG. 4****FIG. 5A**

**FIG. 5B****FIG. 6**

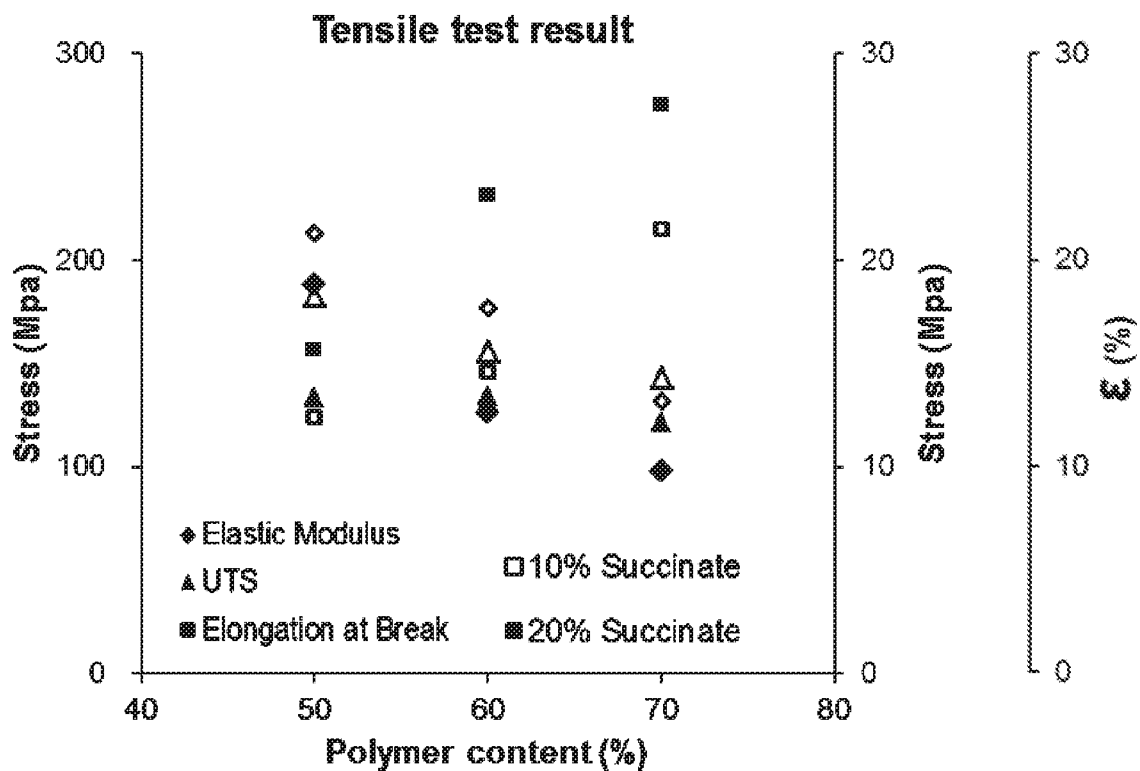
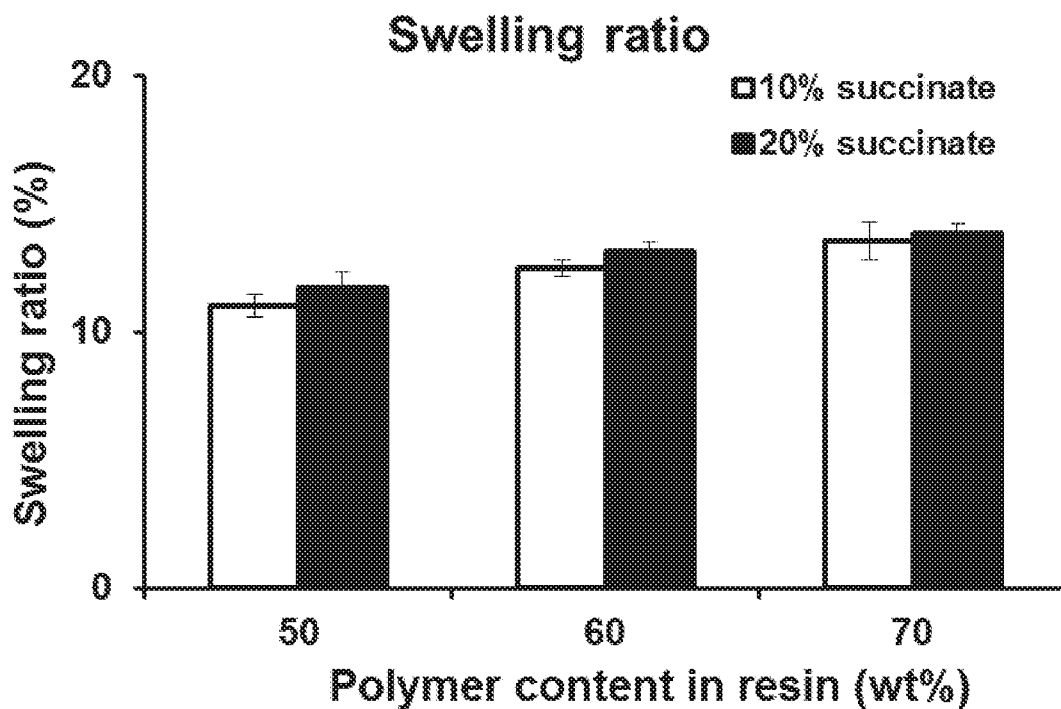
**FIG. 7**

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**FIG. 8A****FIG. 8B**

**FIG. 9****FIG. 10A**

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**FIG. 10B****FIG. 11**

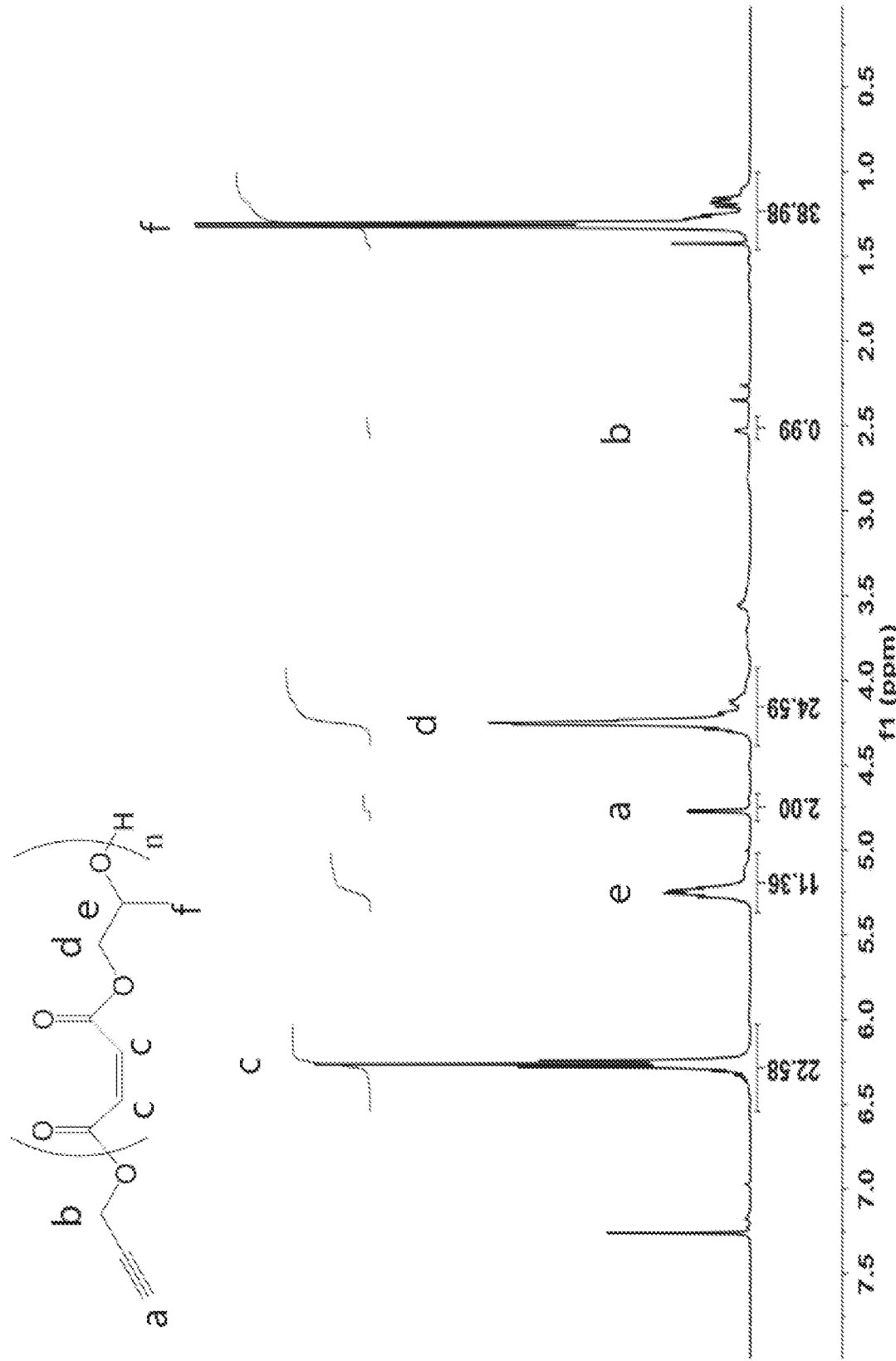
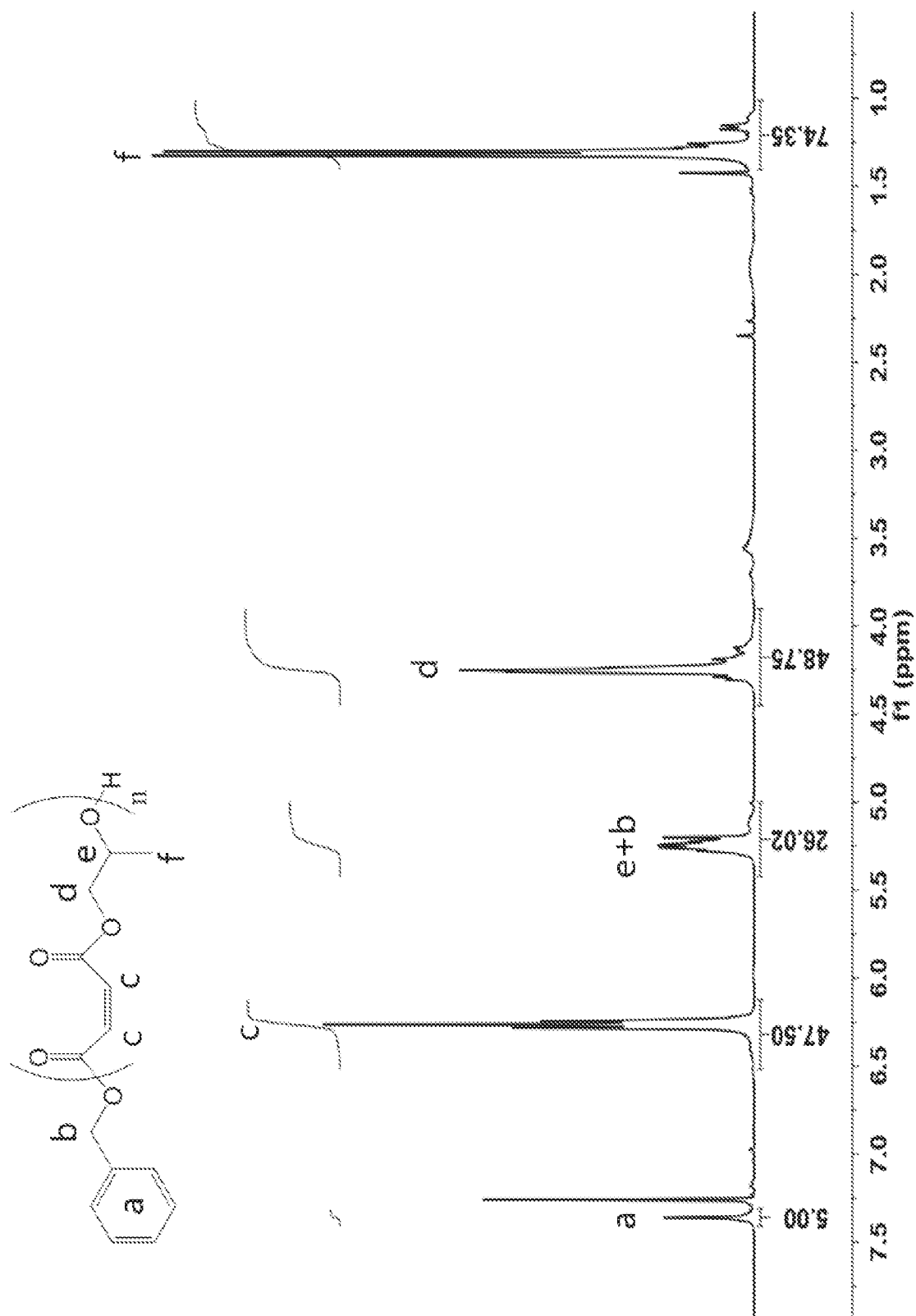


FIG. 12

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**FIG. 13**

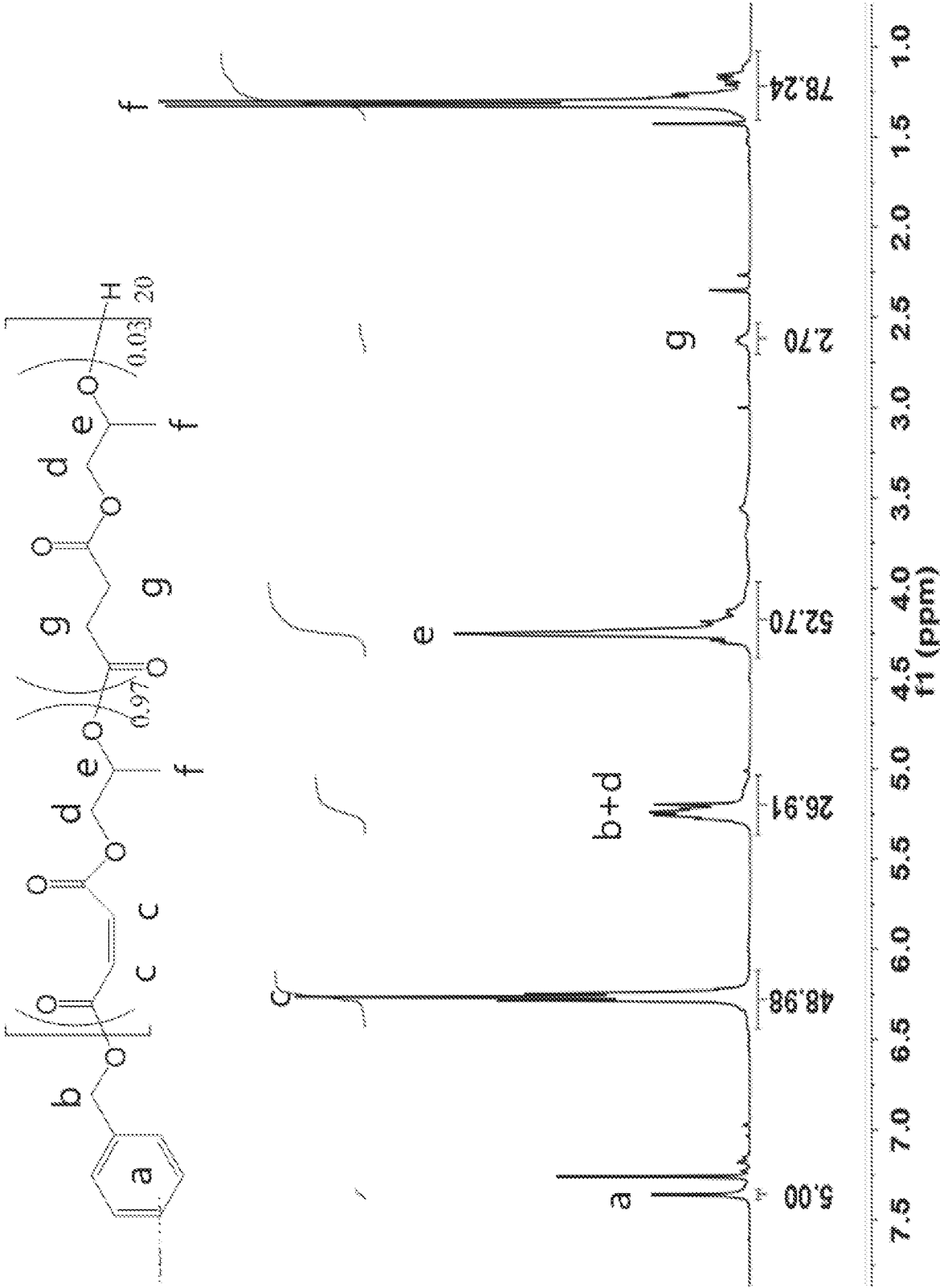
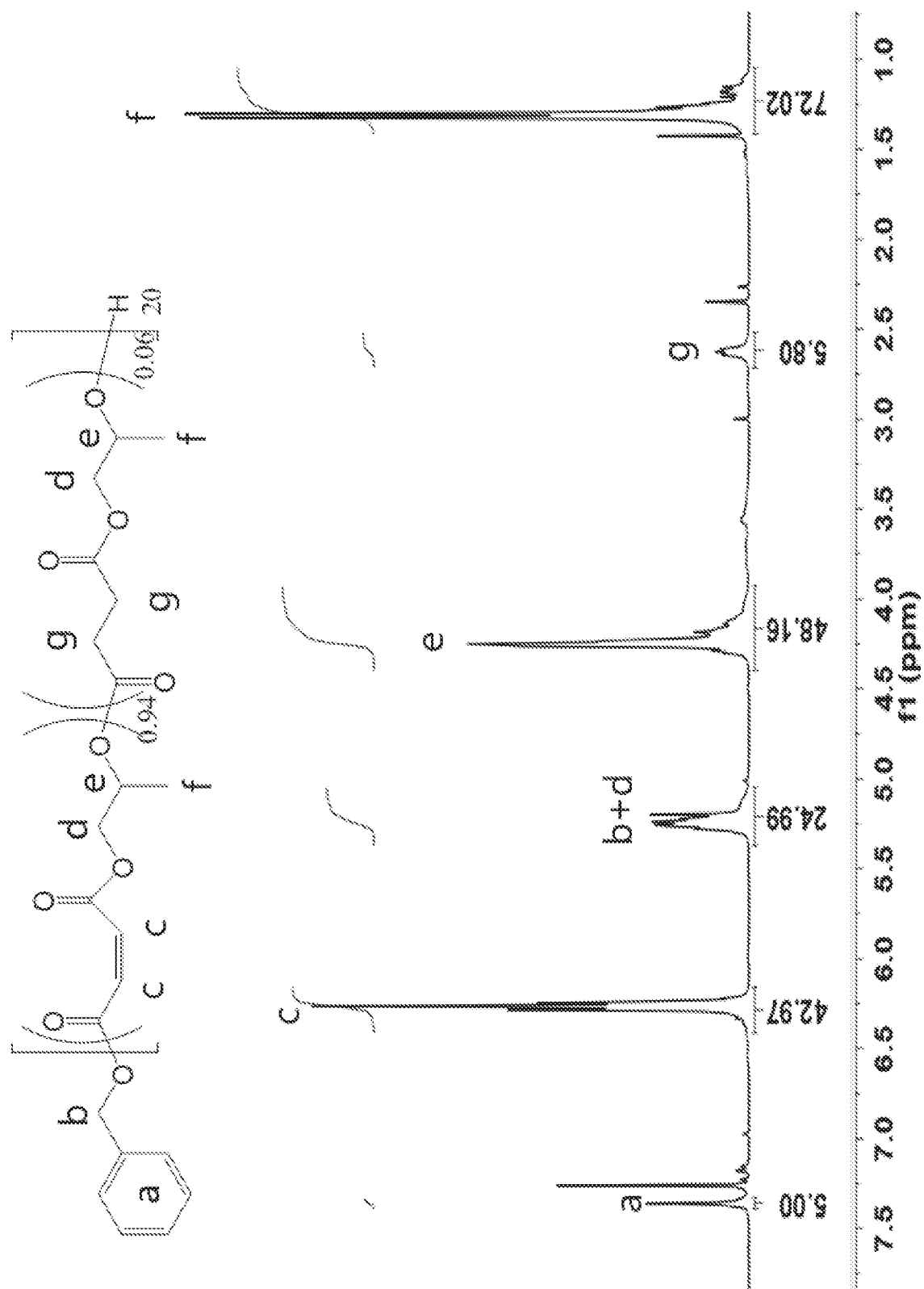


FIG. 14



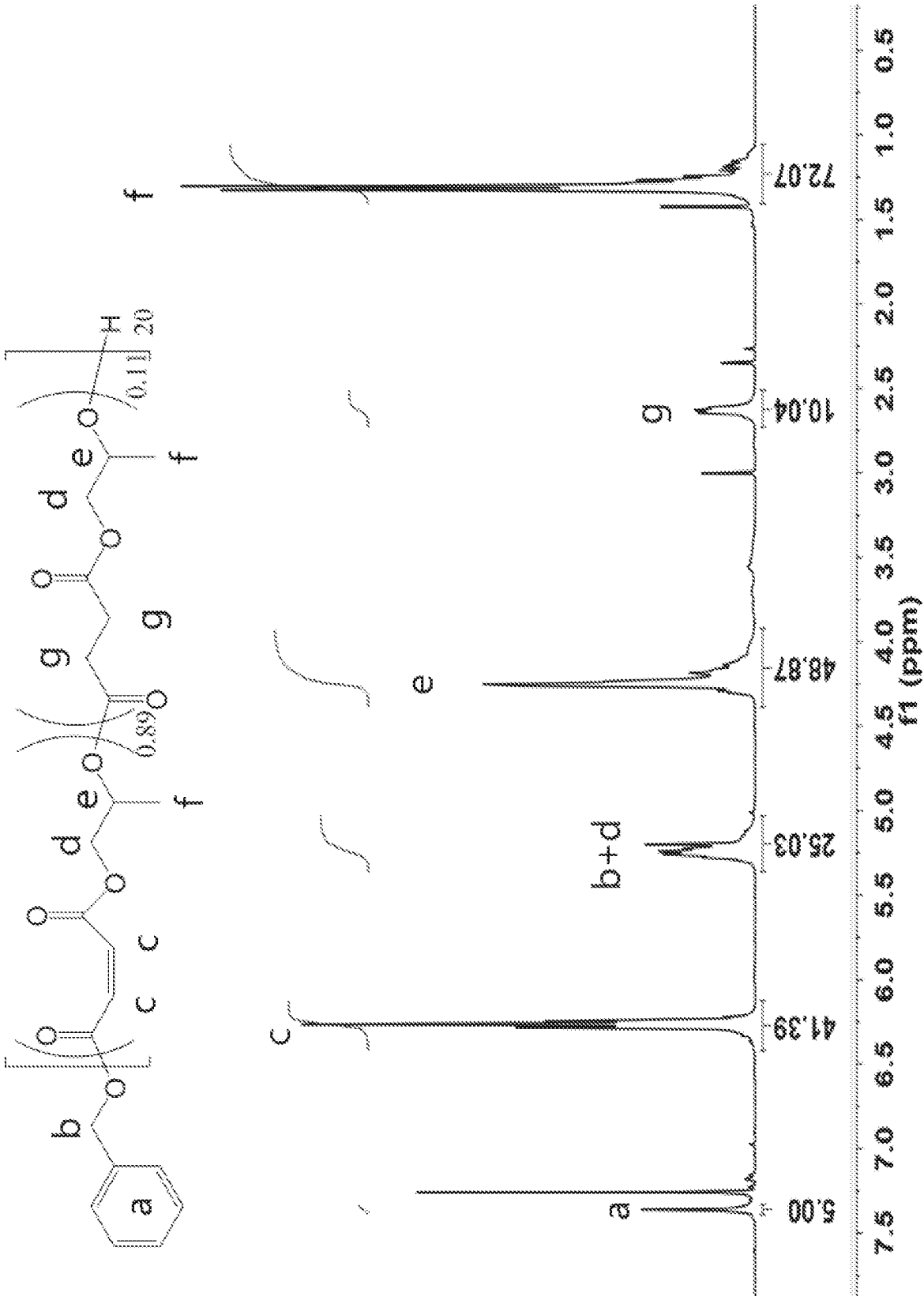


FIG. 16

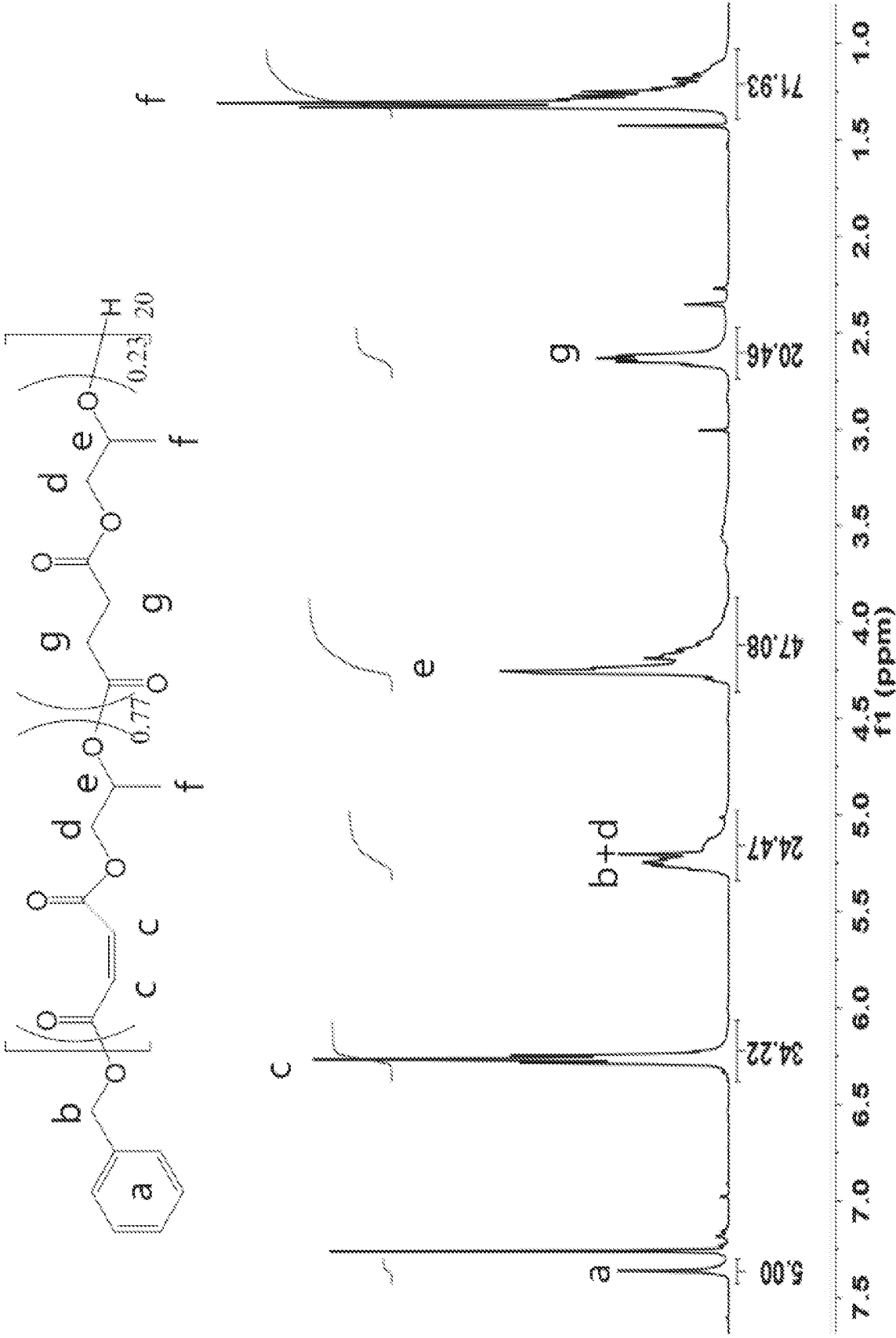


FIG. 17

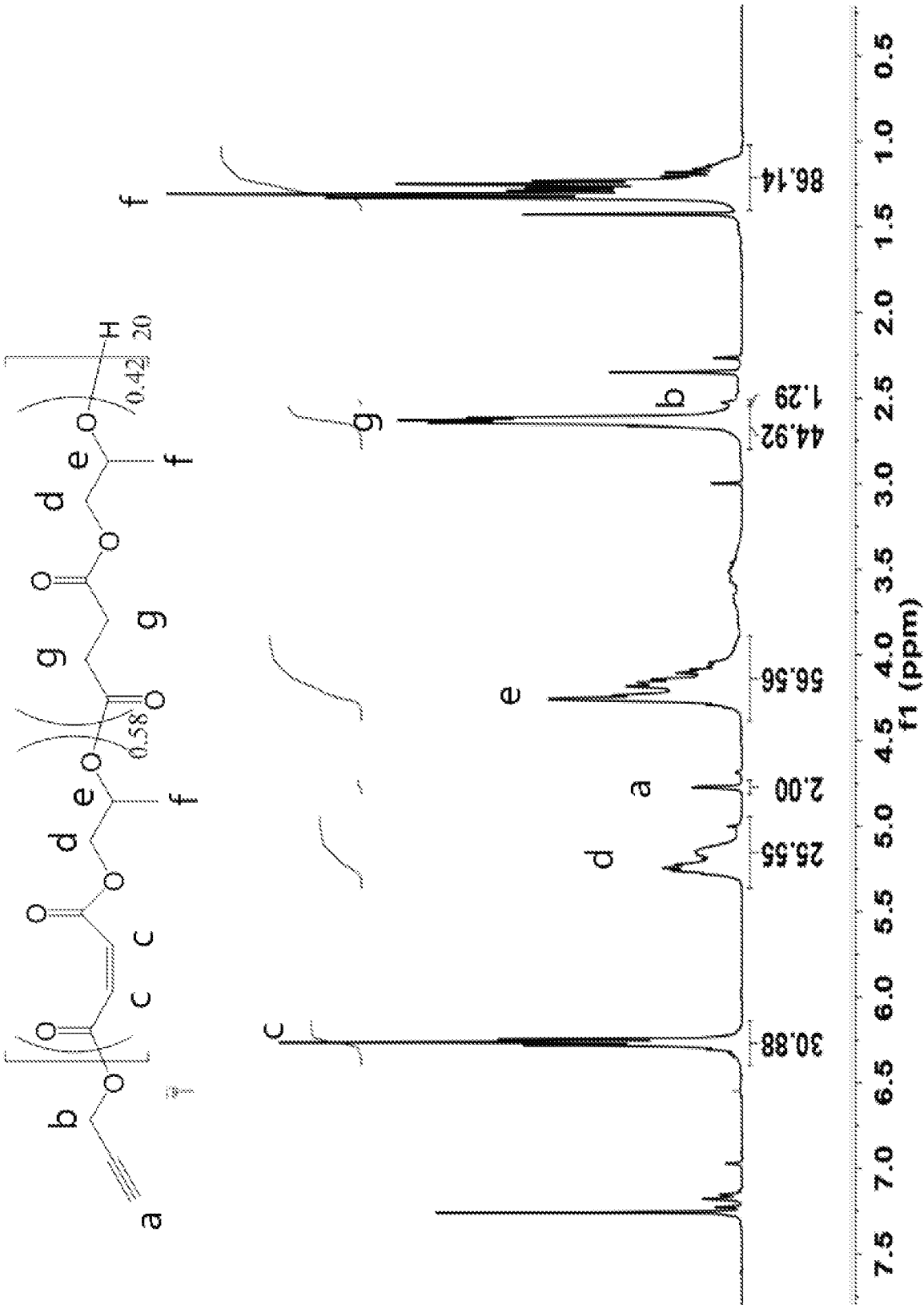
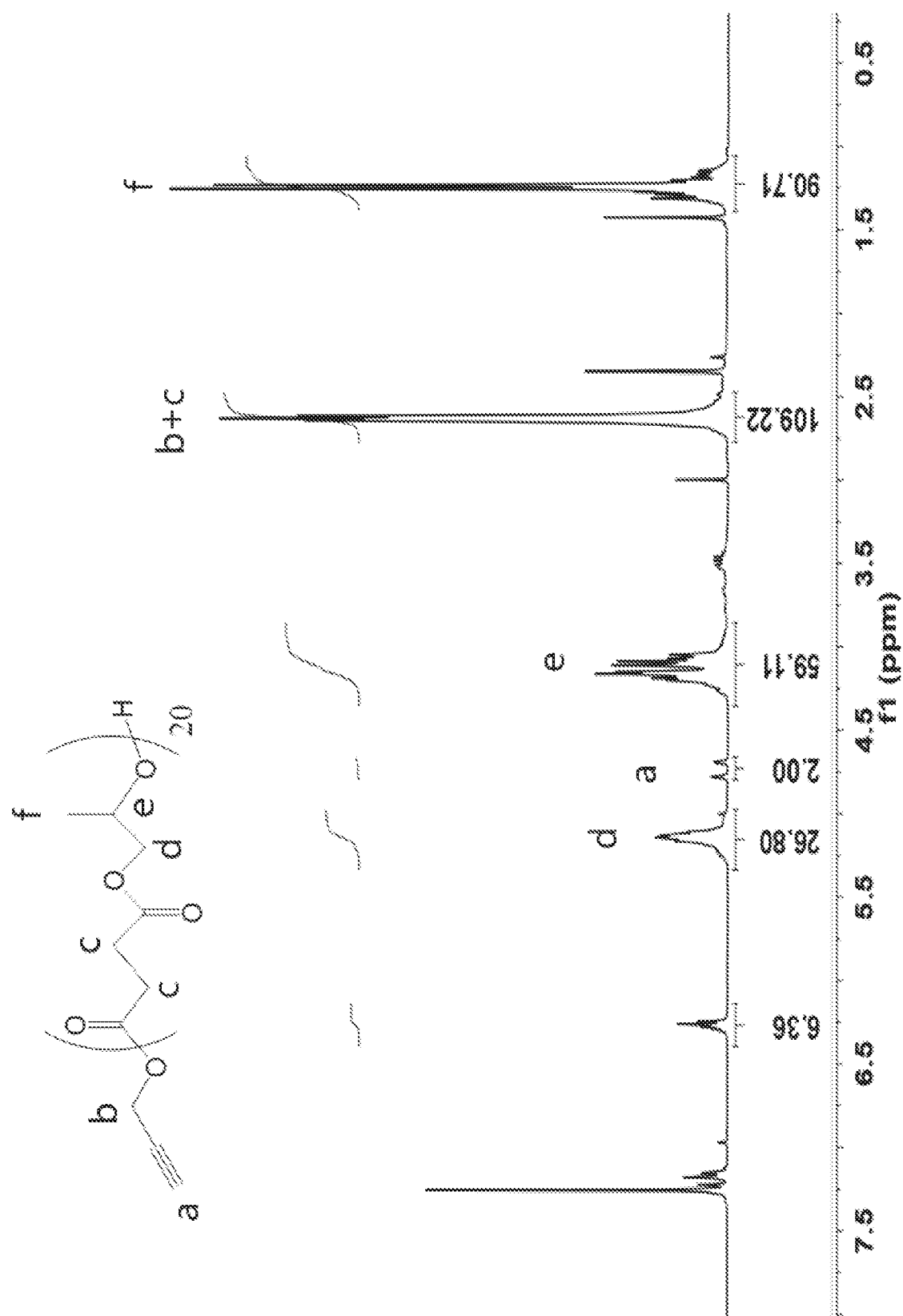


FIG. 18



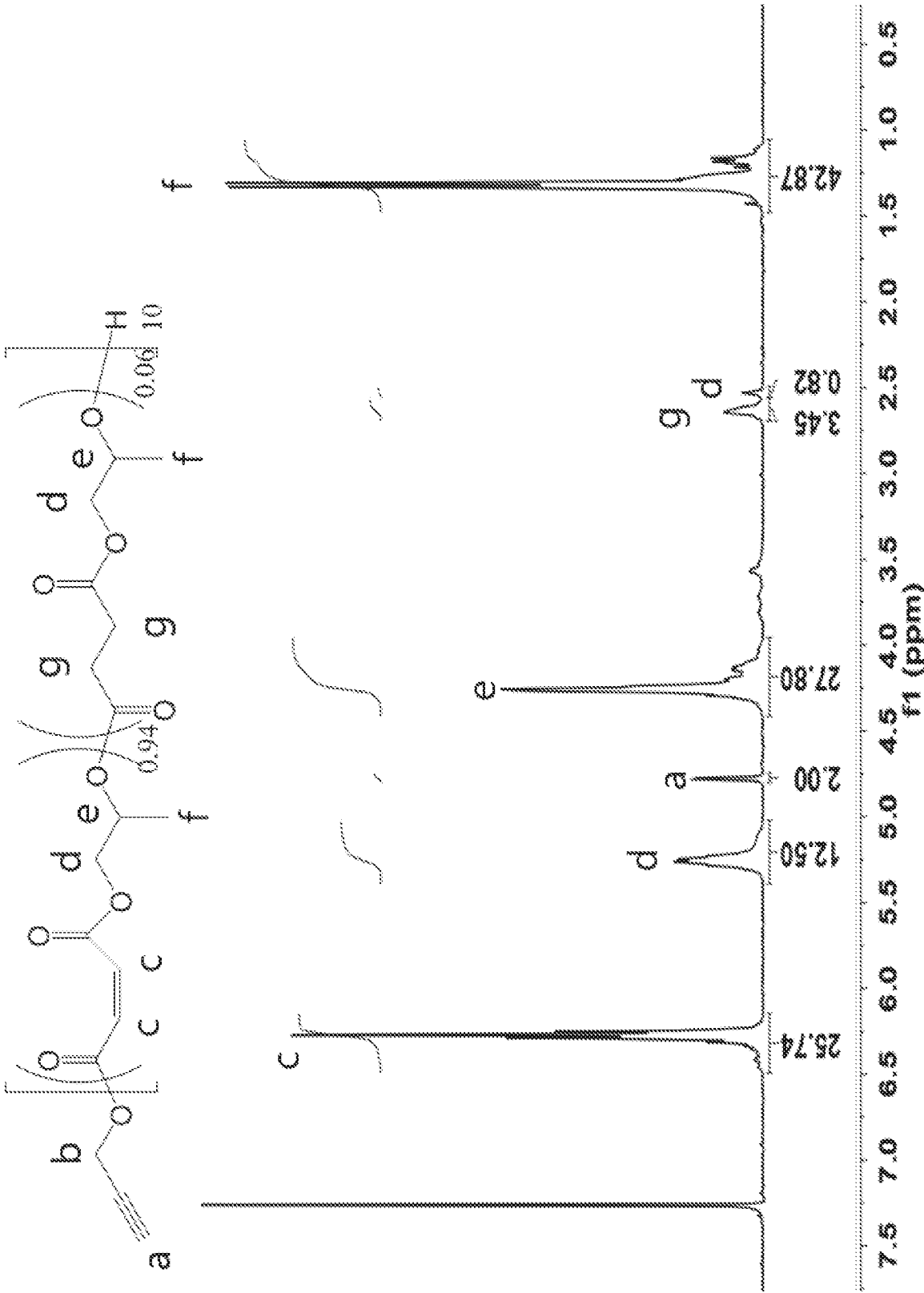
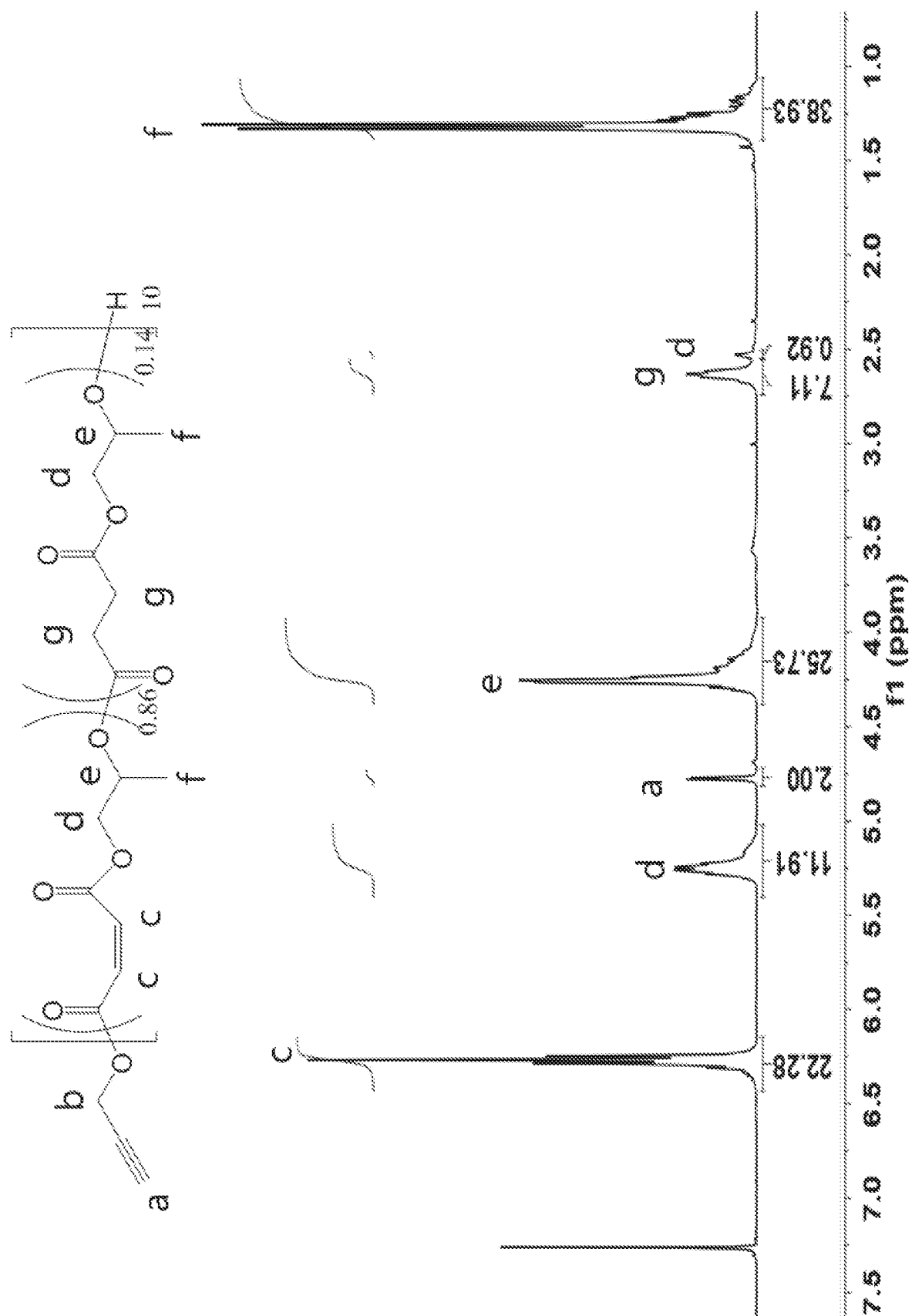


FIG. 20

**FIG. 21**

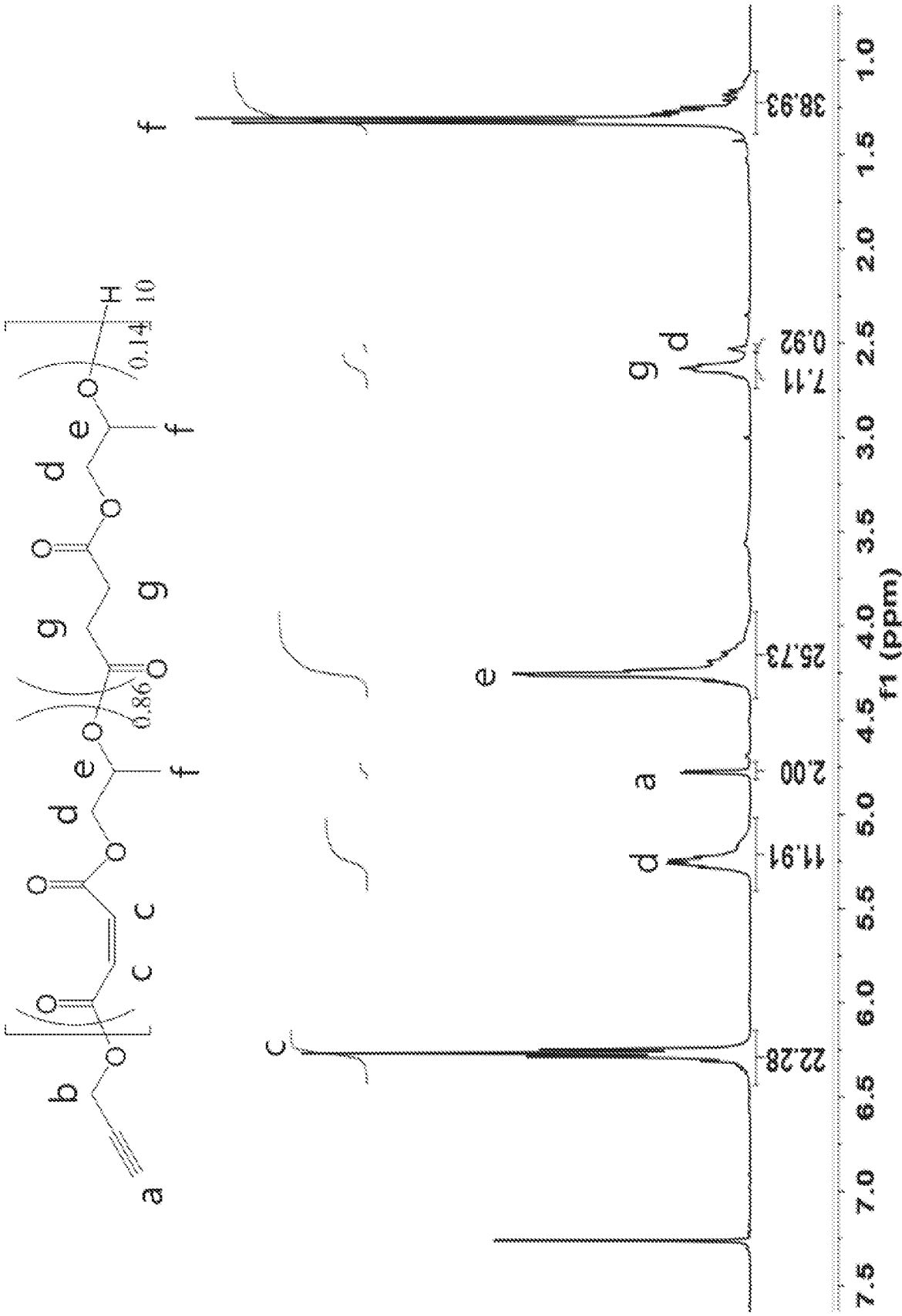


FIG. 22

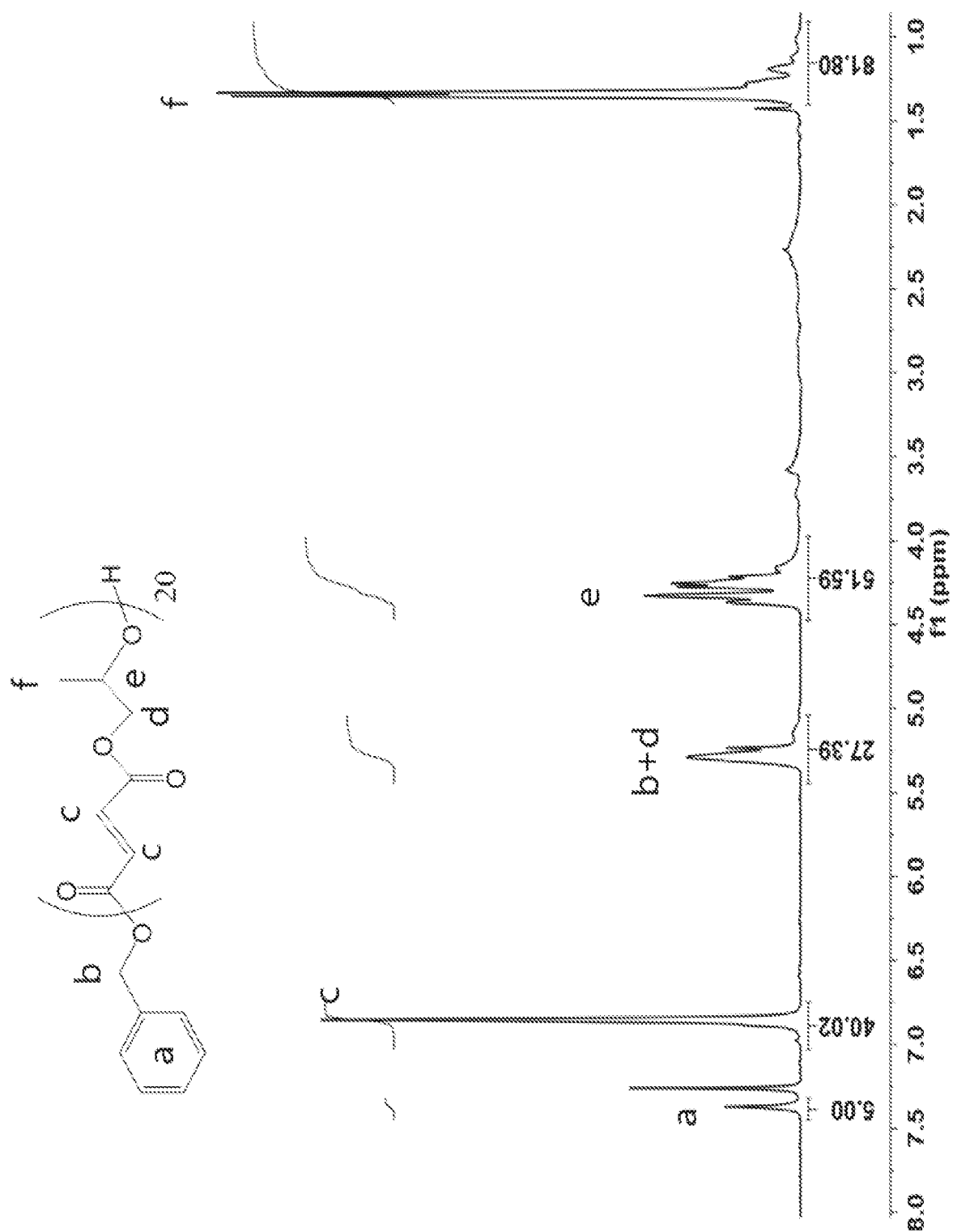


FIG. 23

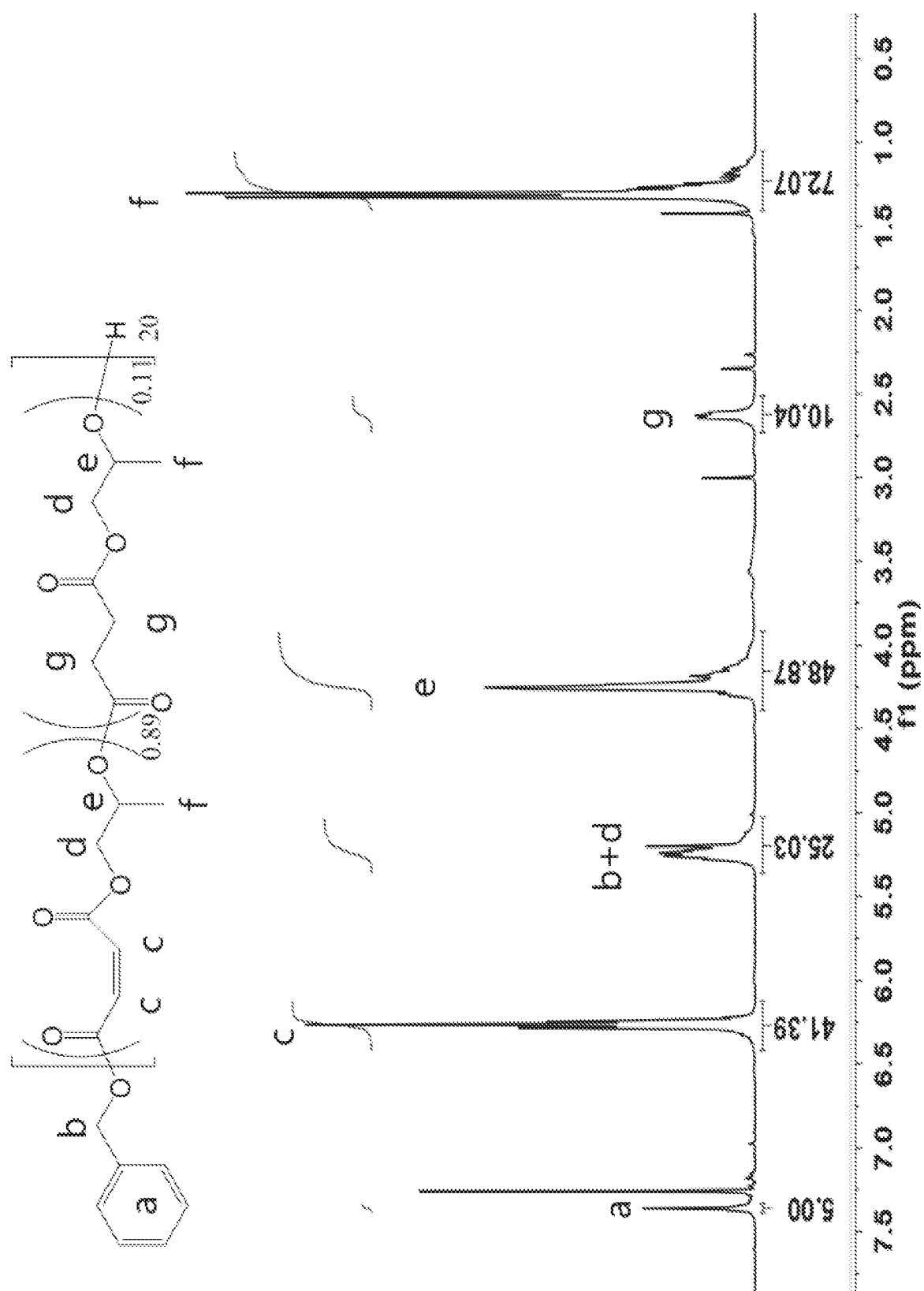


FIG. 24

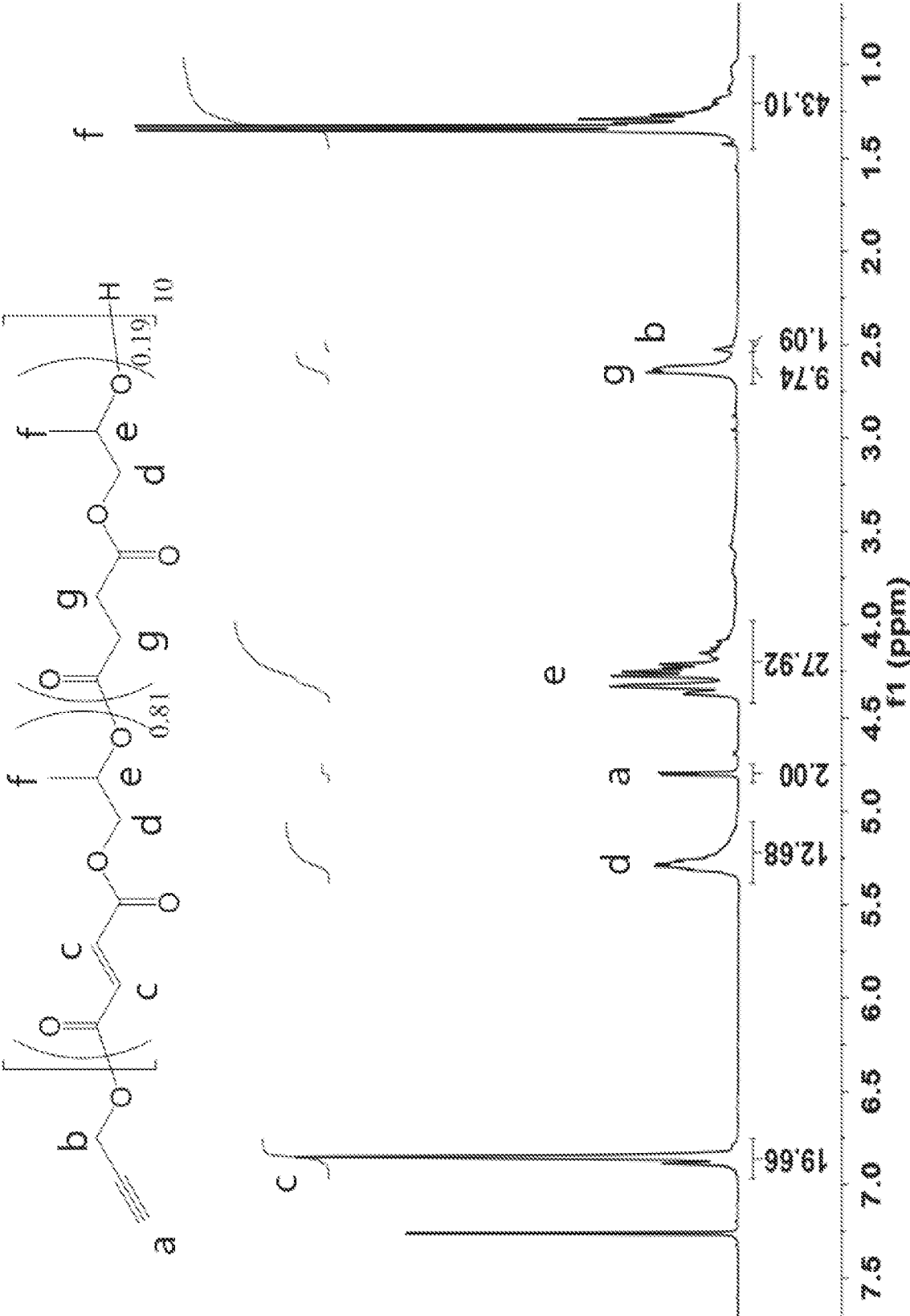


FIG. 25

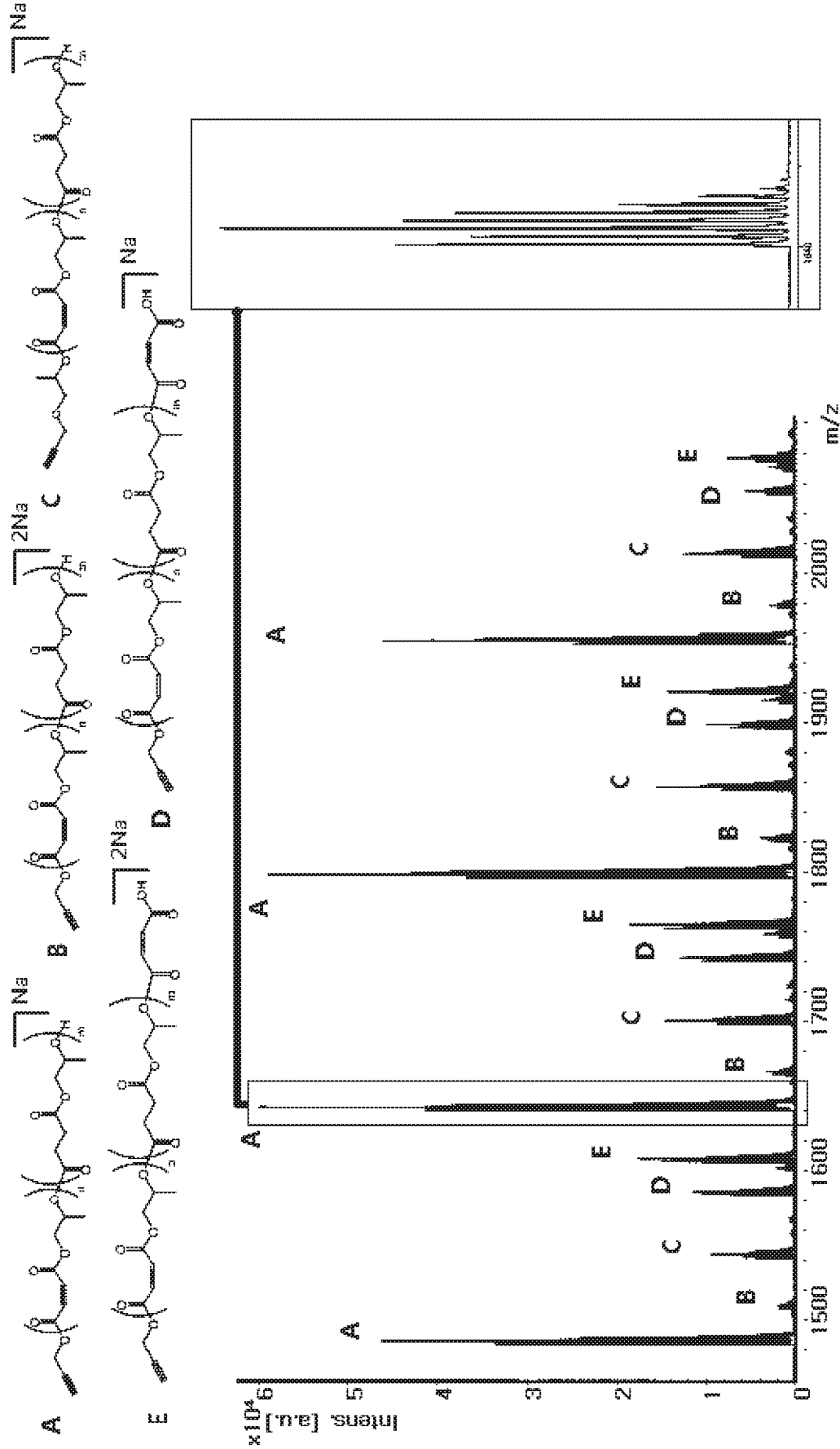


FIG. 26

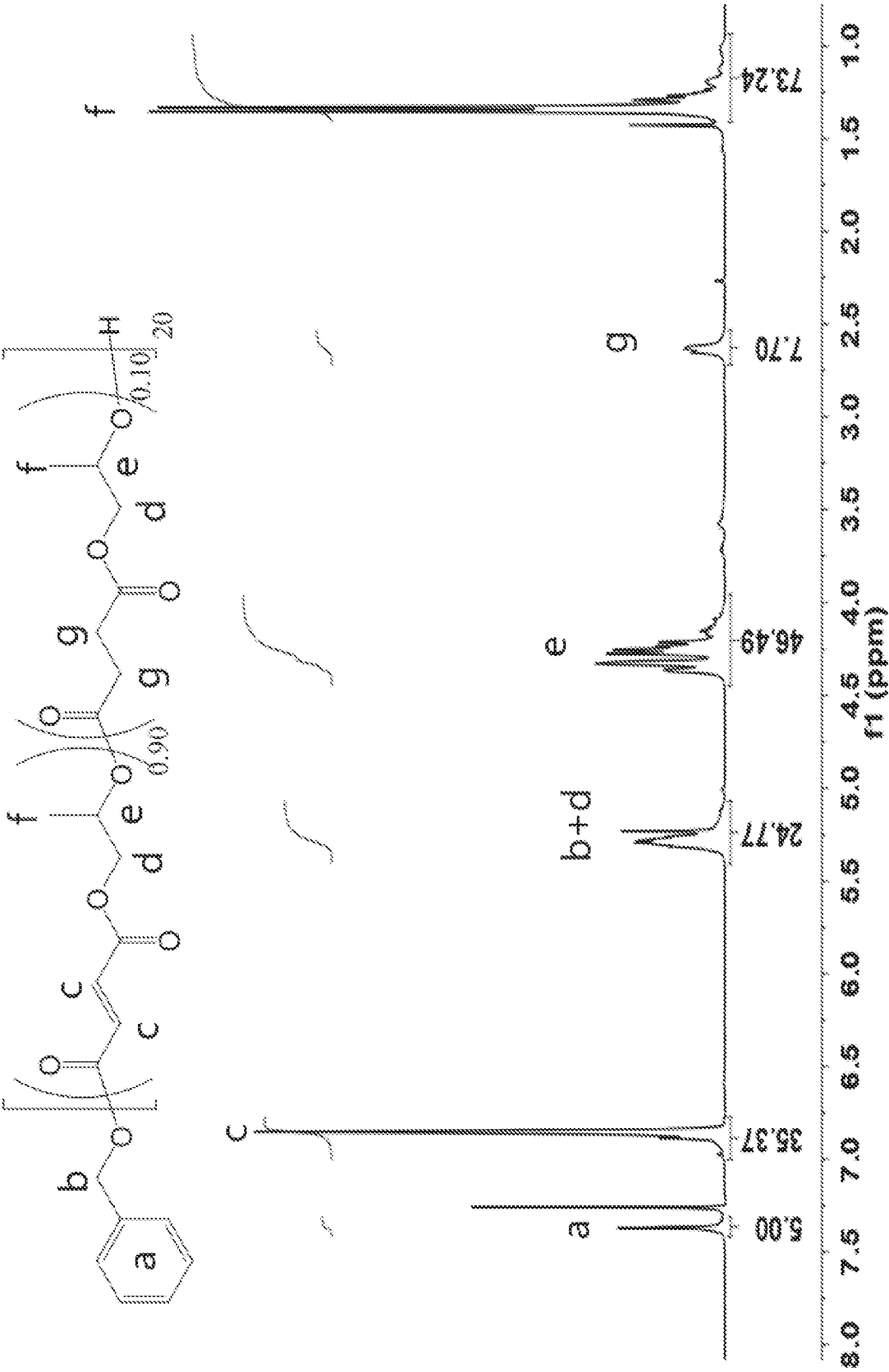


FIG. 27

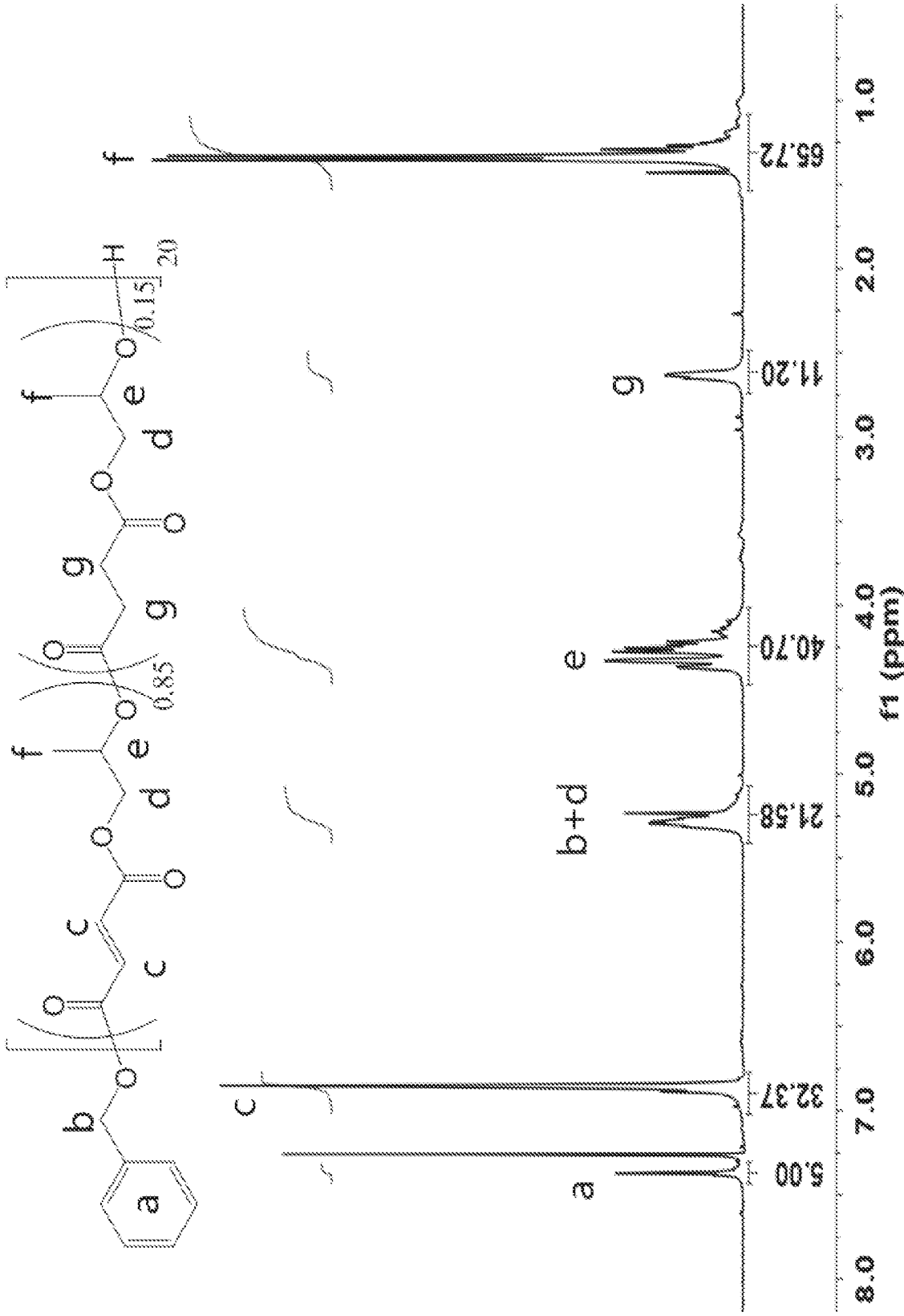


FIG. 28

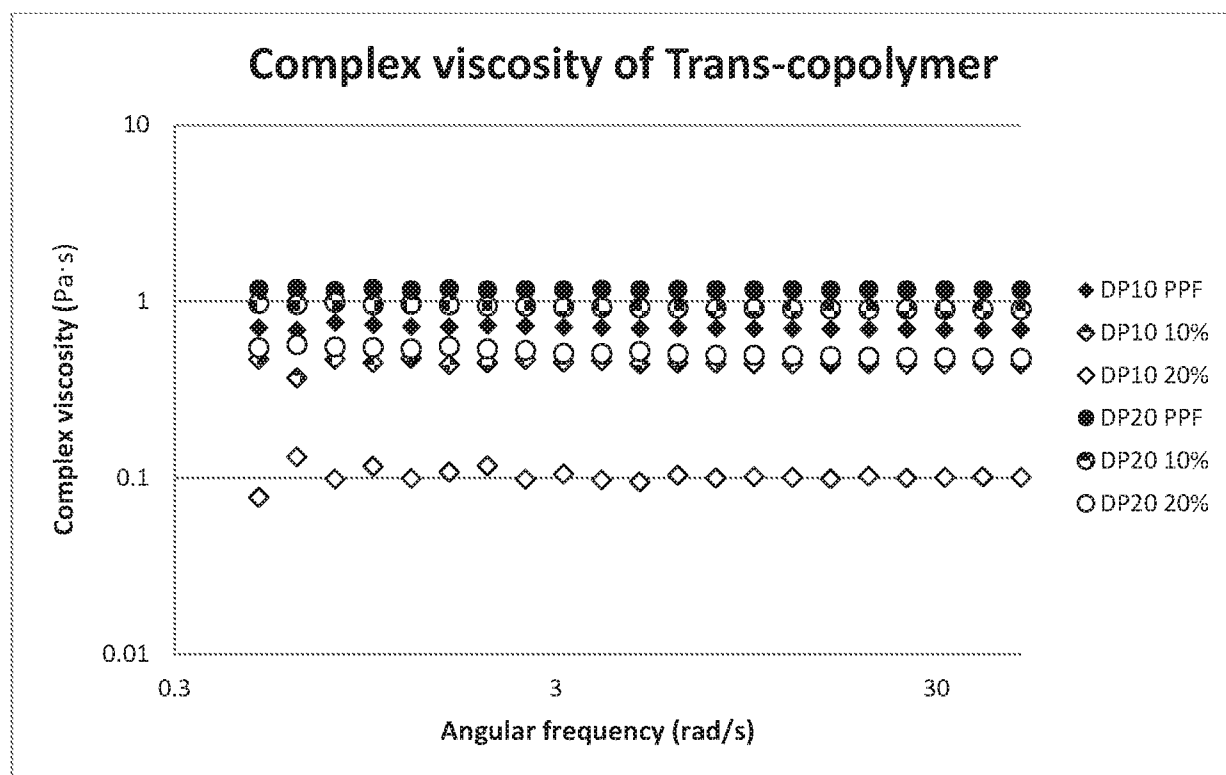
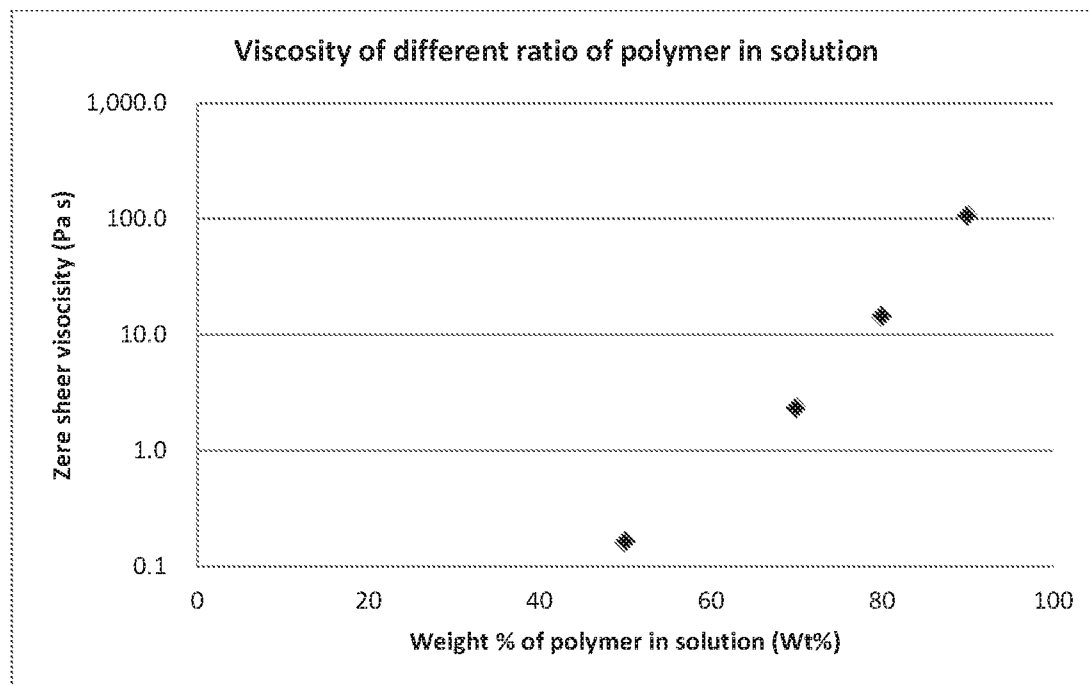
**FIG. 29****FIG. 30**



Fig. 31

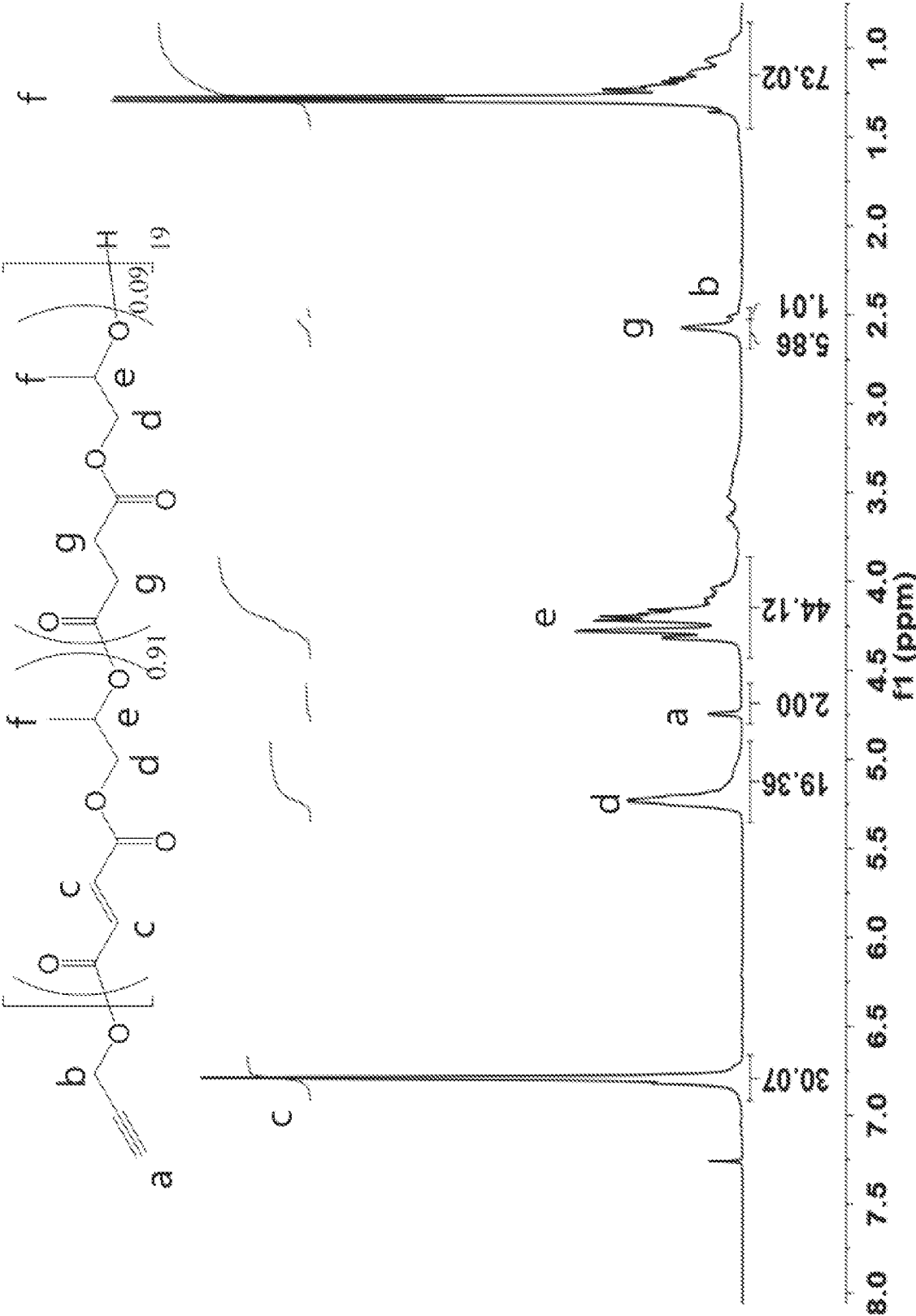
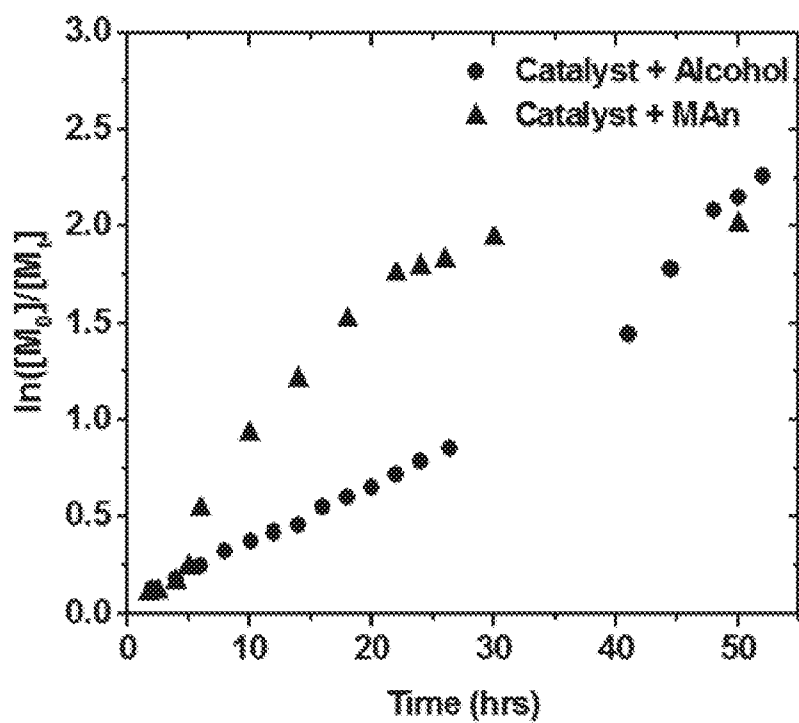
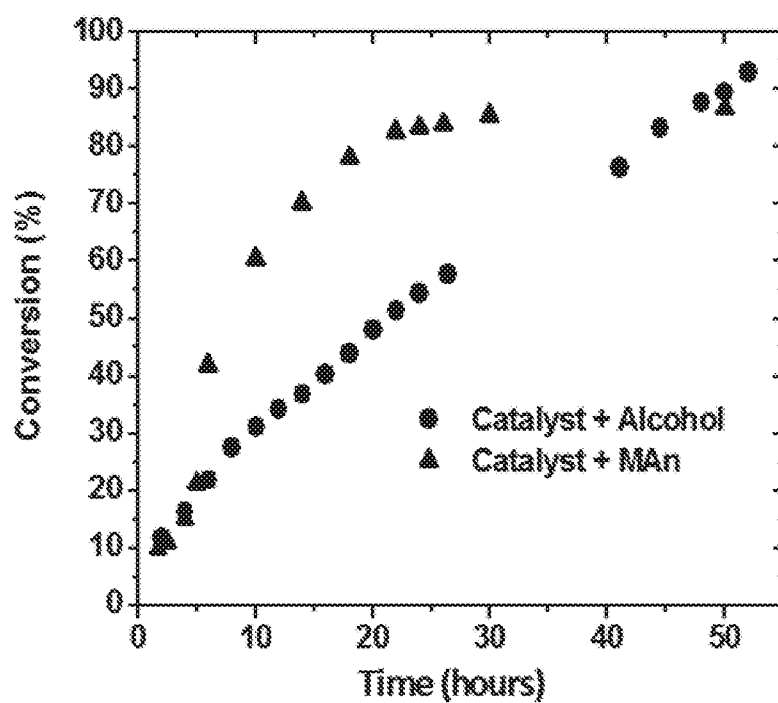
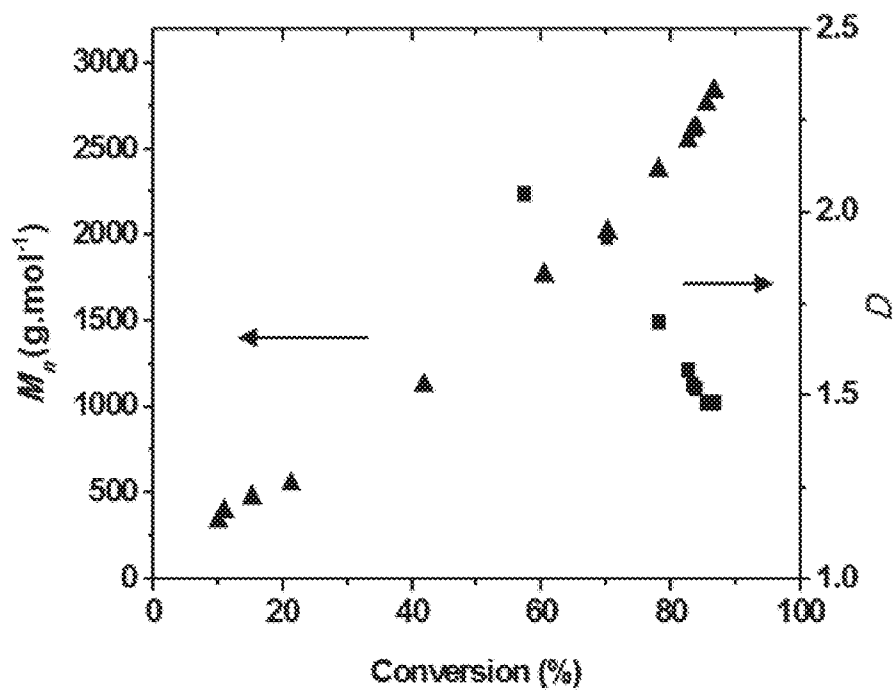
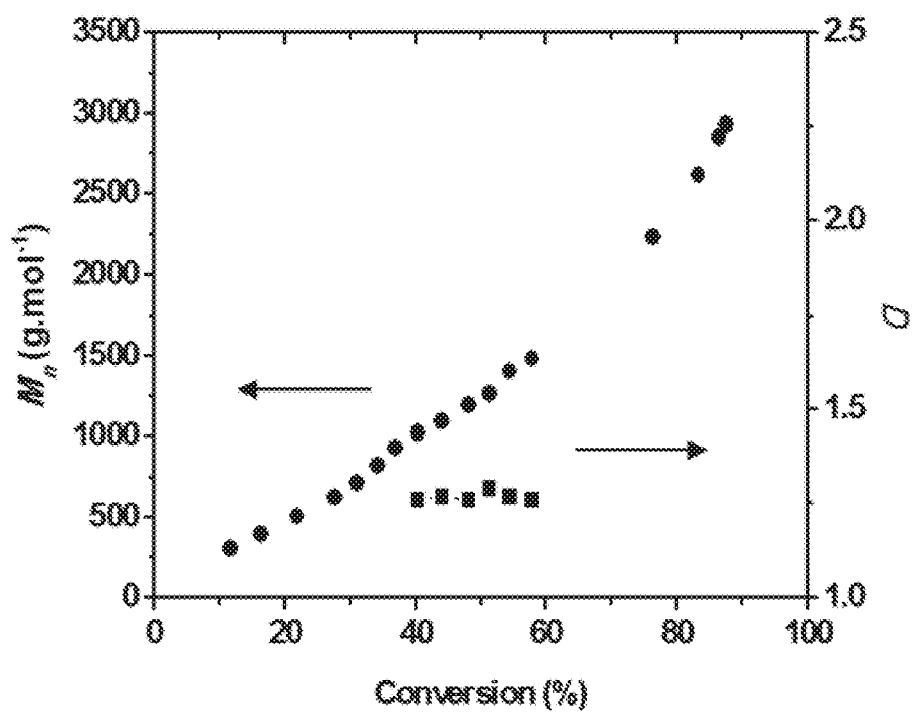


FIG. 32

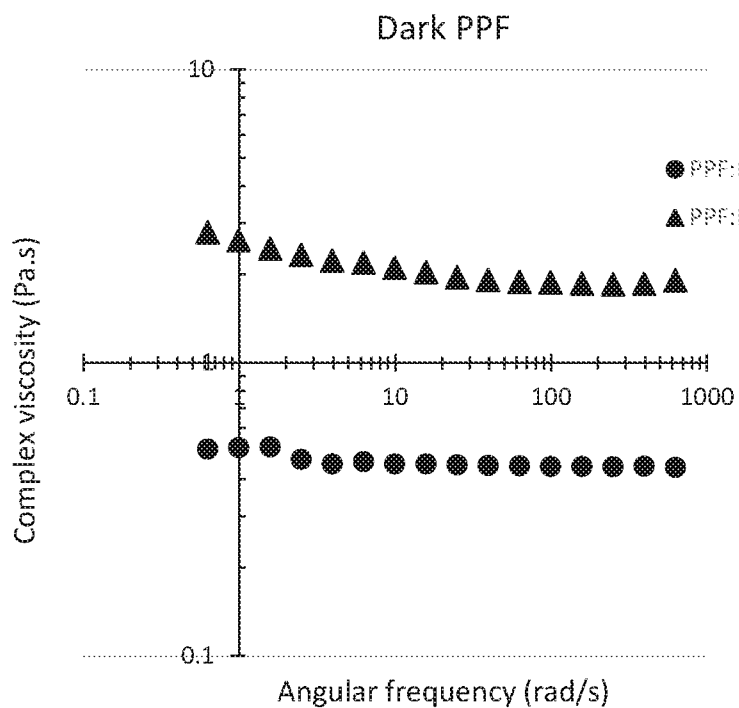
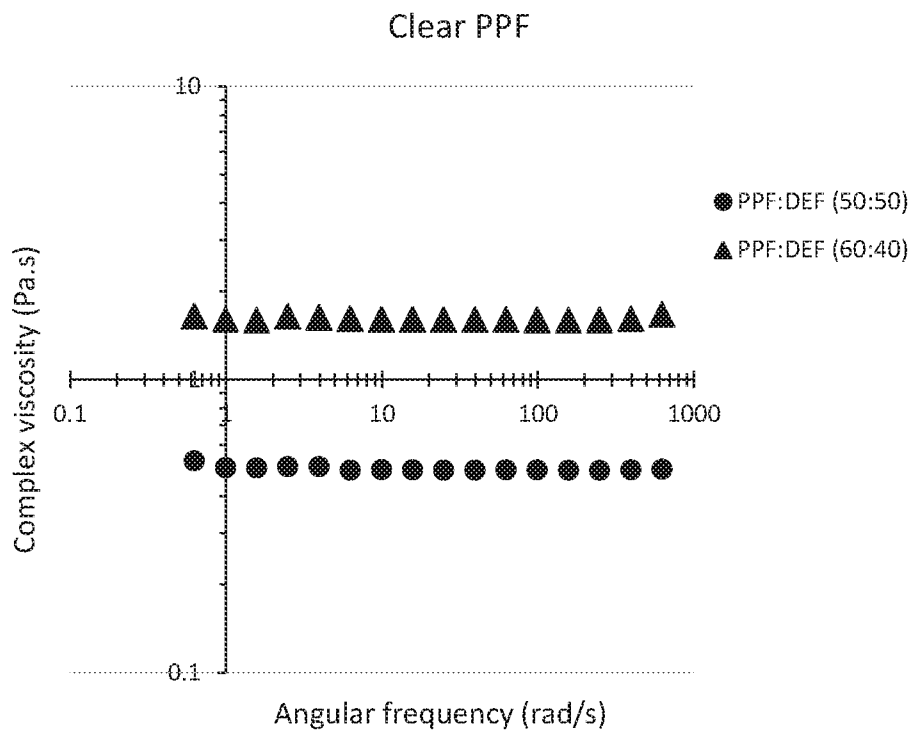
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**FIG. 33A****FIG. 33B**

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**FIG. 33C****FIG. 33D**

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**FIG. 34A****FIG. 34B**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/41782

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - C08G 81/02; C09D 7/12 (2019.01)
 CPC - C08G 63/685; C08G 63/91; C08G 63/912

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 --- A	Sadafule et al. 'Photocrosslinkable unsaturated polyesters from aliphatic diacids', Polymer Photochemistry, January 1982, Vol.2, pages13-21; p14, p15	1-9 ----- 10-19
A	WO 2016/081587 A9 (The University of Akron) 26 May 2016 (26.05.2016); Abstract, para[0070]	10-19
A	Takenouchi et al. 'Effects of Geometrical Difference of Unsaturated Aliphatic Polyesters on Their Biodegradability II. Isomerization of Poly(maleic anhydride-co-propylene oxide) in the Presence of Morpholine', Polymer Journal, 01 January 2002 (01.01.2002), Vol.34, pages36-42; p37	10
A	Wilson et al. 'Magnesium Catalyzed Polymerization of End Functionalized Poly(propylene maleate) and Poly(propylene fumarate) for 3D Printing of Bioactive Scaffolds', Journal of the American Chemical Society, 13 December 2017 (13.12.2017), Vol.140, pages277-284; Abstract, p279	11-19
A	US 4,888,413 A (Domb) 19 December 1989 (19.12.1989); entire document	1-19

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

11 October 2019

Date of mailing of the international search report

13 NOV 2019

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/41782

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.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box

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.:
1-19

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/41782

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

Group I: Claims 1-19 drawn to a polymer composition comprising the one or more isomerized residues of maleic anhydride monomer, one or more residue of succinic anhydride monomer and one or more residues of propylene oxide monomer

Group II: Claims 20-34 drawn to a method of making a polymer for use in 3D printable resins comprising: A) reacting maleic anhydride, succinic anhydride and propylene oxide and an initiating alcohol in the presence of a magnesium catalyst to form a poly(propylene maleate-co-succinate) copolymer intermediate having a maleic anhydride residue containing a cis double bond; and B) isomerizing the cis double bond in said maleic anhydride residue by reacting the poly(maleic anhydride-co-succinic anhydride-co-propylene oxide) polymer intermediate to form a poly(propylene fumarate-co-succinate) copolymer

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

Special Technical Features

Group II requires a method of making a polymer for use in 3D printable resins comprising: A) reacting maleic anhydride, succinic anhydride and propylene oxide and an initiating alcohol in the presence of a magnesium catalyst to form a poly(propylene maleate-co-succinate) copolymer intermediate having a maleic anhydride residue containing a cis double bond; and B) isomerizing the cis double bond in said maleic anhydride residue by reacting the poly(maleic anhydride-co-succinic anhydride-co-propylene oxide) polymer intermediate to form a poly(propylene fumarate-co-succinate) copolymer, not required by Group I

Shared Common Features

Groups I-II share technical feature of a polymer composition comprising the one or more isomerized residues of maleic anhydride monomer, one or more residue of succinic anhydride monomer and one or more residues of propylene oxide monomer.

However, these shared technical feature does not represent a contribution over prior art, because the shared technical feature as being anticipated by the journal article entitled 'Photocrosslinkable unsaturated polyesters from aliphatic diacids' by Sadafule et al. (hereinafter 'Sadafule'). Sadafule discloses a polymer composition comprising the one or more isomerized residues of maleic anhydride monomer, one or more residue of succinic anhydride monomer and one or more residues of propylene oxide monomer (p14, Scheme 1. "General Polyester Chain", "Compound V").

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups. Groups I-II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.