

CATALYST SYSTEMS FOR CATIONIC POLYMERIZATION OF NORBORNENE**CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of U.S. Provisional Application No. 63/520,103, filed August 17, 2023, entitled "Catalyst Systems for Cationic Polymerization of Norbornene", the entirety of which is incorporated by reference herein.

FIELD OF INVENTION

[0002] This application relates to catalyst systems, methods, and compositions, and more particularly, to catalyst systems, methods, and compositions for cationic polymerization of norbornenes.

BACKGROUND

[0003] Norbornene and its derivatives are unique monomers due to their unique cyclic structure and ability to polymerize according to various polymerization methods, such as metathesis, addition, isomerization mechanisms, and the like. Norbornene is a cyclic alkene with a dense three-dimensional structure: a cyclohexene ring with a bridging methylene in the para-position. When polymerizing, either the double bond provides the locus for covalent bonding with ethylene (or other norbornenes) or the cyclohexene ring opens at the double bond, leaving a pentane ring co-planar with the polymer chain.

[0004] Polymerized norbornenes (polynorbornenes) possess good mechanical strength, heat resistance, low birefringence, good membrane properties, and optical transparency, making them very attractive monomers for polymer synthesis. Indeed, at present, there are several commercially available polynorbornenes, such as TOPAS®, TELENE®, ZEONEX®, and the like, based on norbornene derivatives, such as 5-Ethylidene-2-norbornene.

[0005] Cationic polymerization of ENB (polyENB) has been widely studied in the presence of different Lewis acids such as AlCl₃, EtAlCl₂, BF₃, TiCl₄, SnCl₄, Et₂AlCl. However, such cationic polymerization of ENB to date produces only oligomers, including viscous oils and/or low molecular weight products (less than 10,000 daltons number average molecular weight (Mn)). Additionally, cationic polymerization of norbornene derivatives in the presence of boranes have been studied, including B(C₆F₅)₃ in combination with caprylic acid, 1-phenylethanol, or water, which form high molecular weight polymers; however, these systems are known to form gels, which can interfere with downstream chemical products made therefrom.

[0006] In view of the aforementioned low molecular weight oligomers and/or formation of gels, the present disclosure provides a mechanism for producing polyENB possessing high molecular weight, high glass transition temperature, and low unsaturation that do not form gels so as to produce polymer materials that possess desirable mechanical properties and are optically clear for forming various products.

SUMMARY OF INVENTION

[0007] This application relates to catalyst systems, methods, and compositions, and more particularly, to catalyst systems, methods, and compositions for cationic polymerization of norbornenes.

[0008] The present disclosure provides a method including reacting, under reaction conditions: 5-Ethylidene-2-norbornene (ENB) monomers; a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB). A cationic polymerization method comprising: reacting, under reaction conditions: 5-Ethylidene-2-norbornene (ENB) monomers; a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB).

[0009] The present disclosure provides a composition including a catalytic polymerization reaction product of 5-Ethylidene-2-norbornene (ENB) monomers; a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB).

[0010] Any combinations of the various embodiments and implementations disclosed herein can be used in a further embodiment, consistent with the disclosure. These and other aspects and features can be appreciated from the following description of certain embodiments presented herein in accordance with the disclosure and the accompanying drawings and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings. The following figures are included to illustrate certain aspects of the disclosure, and should not be viewed as exclusive configurations. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0012] FIG. 1 shows a gel permeation chromatography curve of a polyENB material produced according to various aspects of the present disclosure.

[0013] FIGS. 2A-2B show differential scanning calorimetry curves for T_g of various polyENB materials produced according to various aspects of the present disclosure.

DETAILED DESCRIPTION

[0014] This application relates to catalyst systems, methods, and compositions, and more particularly, to catalyst systems, methods, and compositions for cationic polymerization of norbornenes.

[0015] In the following detailed description of embodiments of the present disclosure, numerous specific details are set forth in order to provide a more thorough understanding of the claimed subject matter. However, it will be apparent to one of ordinary skill in the art that the embodiments disclosed herein may be practiced without these specific details. In other instances, well-known features have not been described in detail to avoid unnecessarily complicating the description.

[0016] Advantageously, the polyENB produced according to the cationic catalyst systems described herein are characterized as having high molecular weight, suitable (good) mechanical properties, high glass transition temperature, and low unsaturation/low olefin content. Current conventional cationic catalyst systems fail produce only low molecular weight polymers from norbornene monomers, thus lacking in the enhanced qualities of the polyENB produced according to the cationic catalyst systems of the present disclosure.

[0017] The produced polyENB of the present disclosure is optically clear and tough, thereby capable of producing a raw material suitable for use in forming a variety of plastic products. These products can be used as aspects of various specialty and commercial applications, such as within the automotive industry (e.g., under the hood parts), the construction industry, the aviation industry, the electronics industry, the medical industry, the medical and scientific research industries (e.g., optical microscopy), the optometry industry (e.g., glasses lenses), and the 3D printing industry, among others.

[0018] The catalyst systems of the present disclosure utilize (1) trimethylsilylchloride ((CH₃)₃Si-Cl) as a catalyst (initiator) in the presence of (2) a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate (C₂₄BF₂₀Li · 2.5C₄H₁₀O) and (3) an optional polar solvent of methyl chloride (MeCl) or a combination of MeCl and hexane (C₆H₁₄) to catatonically polymerize 5-Ethylidene-2-norbornene (ENB) monomers. In one or more alternative embodiments, the catalyst or co-catalyst may be prepared using a solvent, such as toluene, as provided herein below with respect to the Examples. The optional polar solvent may be used to form free ions to aid in the reactivity of the polymerizing monomer chain. The catalyst systems of the present disclosure may comprise a ratio of norbornene monomers to catalyst in the range of about 400:1 to about 5000:1, encompassing any

value and subset therebetween, such as in the range of about 400:1 to about 1000:1, or about 1000:1 to about 2000:1, or about 2000:1 to about 3500:1, or about 3500:1 to about 5000:1. The catalyst systems of the present disclosure may comprise a ratio of catalyst to co-catalyst of 1:1. The catalyst systems of the present disclosure may comprise a ratio of catalyst to solvent (optional), when included, in the range of about 1:0.2 to about 1:1, encompassing any value and subset therebetween, such as in the range of about 1:0.2 to about 1:0.5, or about 1:0.5 to about 1:1, or about 1:1 to about 1:2, or about 1:2 to about 1:4.

[0019] Polymerization to form polyENB according to the present disclosure may be performed by initially contacting the norbornene monomers with the catalyst, followed by the addition of the co-catalyst and allowed to react for a period of time, as described herein below.

[0020] Polymerization to form polyENB according to the present disclosure may be carried out at polymerization temperatures in the range of about 20°C to about -45°C, encompassing any value and subset therebetween, such as in the range of about 20°C to about 30°C, or about -20°C to about -45°C. The selected polymerization temperature may depend on a number of factors including, for example, the catalyst, the co-catalyst, and the optional solvent selected, as well as their interaction capacity. As used herein, the term “room temperature” or “RT” includes temperatures in the range of about 20°C to about 25°C, encompassing any value and subset therebetween. Polymerization reaction time using the catalyst systems of the present disclosure may be in the range of about 10 minutes (min) to about 90 min, encompassing any value and subset therebetween, such as about 15 min to about 60 min, or about 30 min to about 60 min.

[0021] The resultant cationic polymerized polyENB may have a weight average molecular weight (Mw) in the range of about 50 kilodaltons (kDa) to about 700 kDa, encompassing any value and subset therebetween, such as in the range of about 100 kDa to about 700 kDa, or about 100 kDa to about 200 kDa, or about 300 kDa to about 700 kDa, or about 100 kDa to about 400 kDa. The polyENB may have a number average molecular weight (Mn) in the range of about 45 kDa to about 450 kDa, encompassing any value and subset therebetween, such as in the range of about 45 kDa to about 400 kDa, or about 100 kDa to about 200 kDa, or about 200 kDa to about 450 kDa. The polyENB may have a Z-average molar mass (Mz) in the range of about 100 kDa to about 2,500 kDa, encompassing any value and subset therebetween, such as in the range of about 100 kDa to about 400 kDa, or about 400 kDa to about 1,000 kDa, or about 2,000 kDa to about 2,500 kDa. The Mw, Mn, and Mz according to the present disclosure, unless otherwise indicated, is determined using gel permeation chromatography (GPC).

[0022] The polyENB exhibits suitable (good) glass transition temperature (T_g), which is directly related to its thermal stability and mechanical strength for a given end-use application (product). T_g is the temperature at which an amorphous polymer changes from a brittle “glassy” state to a viscous or rubber state as temperature. The T_g according to the present disclosure, unless otherwise indicated, is measured by Differential Scanning Calorimetry (DSC).

[0023] The polyENB produced according to the catalyst systems of the present disclosure may have a T_g based on ASTM D3418 (2021) in the range of about 100°C to about 250°C, encompassing any value and subset therebetween, such as about 100°C to about 200°C, or about 150°C to about 200°C, or about 100°C to about 150°C, or about 200°C to about 250°C.

[0024] The polyENB of the present disclosure exhibits suitable (good) mechanical properties for use in forming various chemical and specialty products (plastics), as described in brief above. These mechanical properties include tensile strength, Young’s Modulus, and break at strain. The tensile strength according to the present disclosure, unless otherwise indicated, is determined according to ASTM D412 (2021), yielding Young’s Modulus and strain at break values.

[0025] Tensile strength is a measure of the force required to break a polymer sample specimen and the extent to which the specimen stretches or elongates to a breaking point. The force is applied by controlled tension.

[0026] The polyENB described herein formed using the catalyst systems of the present disclosure may have a tensile strength at maximum load in the range of about 15 mPa to about 30 mPa, encompassing any value and subset therebetween, such as about 15 mPa to about 25 mPa, or about 20 mPa to about 30 mPa, or about 20 mPa to about 25 mPa.

[0027] Young’s Modulus (also referred to as modulus of elasticity) is a mechanical property that describes the tensile or compressive stress of a solid material (polymer) when force is applied lengthwise. Young’s Modulus quantifies the relationship between tensile stress σ (force per unit area) divided by axial strain ϵ (proportional deformation) in the linear elastic region of a material.

[0028] In various embodiments, the polyENB produced using the catalyst systems of the present disclosure may be characterized by having high values for Young’s Modulus. In non-limiting examples, the polyENB may have a Young’s Modulus in the range of about 2,000 megapascals (MPa) to about 3,000 mPa, encompassing any value and subset therebetween, such as about 2,000 MPa to about 2,500 MPa, or about 2,500 mPa to about 3,000 mPa.

[0029] Strain at break is determined based on tensile strength testing and may also be referred to as fracture strain or tensile elongation at break. It is a measure of the percentage (%) increase in length of a sample (polymer) that will achieve breaking.

5 [0030] In one or more aspects of the present disclosure, the polyENB produced according to the catalyst systems described herein have strain at break values in the range of about 1% to about 5%, encompassing any value and subset therebetween, such as about 1% to about 1.5%, or about 1.5% to about 2.5%, or about 3% to about 5%.

10 [0031] In one or more aspects of the present disclosure, the polyENB produced according to the catalysts systems described herein may have an olefinic proton content (mol%) of less than 5% or less than 3%, or in the range of about 1% to about 5%, encompassing any value and subset therebetween.

[0032] Although the present disclosure is described particularly with reference to ENB monomers, it is to be appreciated that other norbornene monomers may be used in accordance with the present disclosure to produce a polynorbornene, without departing from the scope of the present disclosure.
15 Examples of such monomers include, but are not limited to, norbornadiene-2,5 (NBD), 5-vinyl-2-norbornene (VNB), dicyclopentadiene (DCPD), and 5-methylene-2-norbornene (MNB).

[0033] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the present specification and associated claims are to be understood as being modified in all instances by the term "about." Accordingly,
20 unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the incarnations of the present inventions. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claim, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying
25 ordinary rounding techniques.

[0034] One or more illustrative incarnations incorporating one or more invention elements are presented herein. Not all features of a physical implementation are described or shown in this application for the sake of clarity. It is understood that in the development of a physical embodiment incorporating one or more elements of the present invention, numerous implementation-specific
30 decisions must be made to achieve the developer's goals, such as compliance with system-related, business-related, government-related and other constraints, which vary by implementation and from time to time. While a developer's efforts might be time-consuming, such efforts would be,

nevertheless, a routine undertaking for those of ordinary skill in the art and having benefit of this disclosure.

[0035] While compositions and methods are described herein in terms of “comprising” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps.

[0036] Nonlimiting Example Embodiments

[0037] Embodiments disclosed herein include:

[0038] Embodiment A: A cationic polymerization method comprising: reacting, under reaction conditions: 5-Ethylidene-2-norbornene (ENB) monomers; a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB).

[0039] Embodiment B: A composition comprising: a catalytic polymerization reaction product of: 5-Ethylidene-2-norbornene (ENB) monomers; a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB).

[0040] Embodiment C: A cationic polymerization method comprising: reacting, under reaction conditions: norbornene monomers selected from the group consisting of 5-Ethylidene-2-norbornene (ENB), norbornadiene-2,5 (NBD), 5-vinyl-2-norbornene (VNB), dicyclopentadiene (DCPD), 5-methylene-2-norbornene (MNB); a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a polynorbornene.

[0041] Embodiment D: A composition comprising: a catalytic polymerization reaction product of: norbornene monomers selected from the group consisting of 5-Ethylidene-2-norbornene (ENB), norbornadiene-2,5 (NBD), 5-vinyl-2-norbornene (VNB), dicyclopentadiene (DCPD), 5-methylene-2-norbornene (MNB); a catalyst trimethylsilylchloride; a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and an optional polar solvent, thereby producing a polynorbornene.

[0042] Embodiments A may have one or more of the following additional elements in any combination:

[0043] Element 1: wherein the reaction conditions comprise a reaction temperature in the range of about 20°C to about 45°C.

- [0044] Element 2: wherein the reaction conditions comprise a reaction time in the range of about 10 minutes to about 90 minutes.
- [0045] Element 3: further comprising initially reacting the ENB monomers and the trimethylsilylchloride catalyst under the reaction conditions for about 1 minute.
- 5 [0046] Element 4: wherein the polar solvent is present and selected from the group consisting of methyl chloride, hexane, and any combination thereof.
- [0047] Element 5: wherein the polar solvent is present and is methyl chloride.
- [0048] Element 6: wherein the polyENB has a weight average molecular weight in the range of about 50 kilodaltons to about 700 kilodaltons.
- 10 [0049] Element 7: wherein the polyENB has a glass transition temperature in the range of about 100°C to about 250°C.
- [0050] Element 8: wherein the polyENB has a tensile strength in the range of about 15 megapascals to about 30 megapascals.
- [0051] Element 9: wherein the polyENB has a Young's Modulus in the range of about 2,000
- 15 megapascals to about 3,000 megapascals.
- [0052] Element 10: wherein the polyENB has a strain at break in the range of about 1% to about 5%.
- [0053] Element 11, wherein the polyENB has an olefinic proton content of less than about 5 mol%.
- [0054] Embodiment A may include any one, more, or all of Elements 1-11, without limitation.
- 20 Without being bound by theory, it is believed that Element C may include any one, more, or all of Elements 1-11, without limitation, with respect to the polynorborene generally (i.e., regardless of the particular norbornene monomer(s) selected.
- [0055] Embodiment B may include any one, more, or all of Elements 4-11, without limitation. Without being bound by theory, it is believed that Element D may include any one, more, or all of
- 25 Elements 4-11, without limitation, with respect to the polynorborene generally (i.e., regardless of the particular norbornene monomer(s) selected.
- [0056] To facilitate a better understanding of the embodiments of the present invention, the following examples of preferred or representative embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

EXAMPLES

[0057] **EXAMPLE 1:** In this Example, cationic polymerization according to the present disclosure was carried out in the presence or absence of a polar solvent of MeCl. Four separate samples (T1-T4) were prepared comprising the below compositions provided in Table 1:

TABLE 1

Component	Sample			
	T1	T2	T3	T4
Norbornene Monomers (g)	9.1	9.0	14.3	14.4
(CH ₃) ₃ Si-Cl Catalyst (μL)	3.2	3.2	6.4	6.4
C ₂₄ BF ₂₀ Li · 2.5C ₄ H ₁₀ O Co-Catalyst (μL)	80 (0.15M)	100 (0.15 M)	200 (0.15 M)	200 (0.15 M)
MeCl Solvent	N/A	N/A	N/A	N/A
Polymerization Conversion (%)	0.5	4.2	1.0	6.6

[0058] **T1 Polymerization Parameters:** Polymerization was performed in a test tube, which was pre-weighed and had a weight of 12.8 g. The (CH₃)₃Si-Cl catalyst was added to the norbornene monomers and allowed to react for about 1 min in a tube. Thereafter, the C₂₄BF₂₀Li · 2.5C₄H₁₀O co-catalyst was added to the tube for a reaction time of about 15 min at RT. After, the polymerization was ceased by the addition of IPA. The precipitated polymer was separated, re-dissolved, dried, and tested as described below. The weight of the recovered polymer in combination with the test tube weight was 12.9 g, giving the recovered polymer a weight of 0.05 g.

[0059] **T2 Polymerization Parameters:** Polymerization was performed in a test tube, which was pre-weighed and had a weight of 12.8 g. The (CH₃)₃Si-Cl catalyst was added to the norbornene monomers and allowed to react for about 1 min in a tube. Thereafter, the C₂₄BF₂₀Li · 2.5C₄H₁₀O co-catalyst and MeCl solvent was added to the tube for a reaction time of about 60 min at RT. After, the polymerization was ceased by the addition of IPA. The precipitated polymer was separated, re-dissolved, dried, and tested as described below. The weight of the recovered polymer in combination with the test tube weight was 13.2 g, giving the recovered polymer a weight of 0.4 g.

[0060] T3 Polymerization Parameters: Polymerization was performed in a test tube, which was pre-weighed and had a weight of 12.8 g. The $(\text{CH}_3)_3\text{Si-Cl}$ catalyst was added to the norbornene monomers and allowed to react for about 1 min in a tube. Thereafter, the $\text{C}_{24}\text{BF}_{20}\text{Li} \cdot 2.5\text{C}_4\text{H}_{10}\text{O}$ co-catalyst was added to the tube for a reaction time of about 16 min at RT. After, the polymerization was ceased by the addition of IPA. The precipitated polymer was separated, re-dissolved, dried, and tested as described below. The weight of the recovered polymer in combination with the test tube weight was 13.0 g, giving the recovered polymer a weight of 0.1 g.

[0061] T4 Polymerization Parameters: Polymerization was performed in a test tube, which was pre-weighed and had a weight of 12.8 g. The $(\text{CH}_3)_3\text{Si-Cl}$ catalyst was added to the norbornene monomers and allowed to react for about 1 min in a tube. Thereafter, the $\text{C}_{24}\text{BF}_{20}\text{Li} \cdot 2.5\text{C}_4\text{H}_{10}\text{O}$ co-catalyst was added to the tube for a reaction time of about 60 min at RT. After, the polymerization was ceased by the addition of IPA. The precipitated polymer was separated, re-dissolved, dried, and tested as described below. The weight of the recovered polymer in combination with the test tube weight was 13.8 g, giving the recovered polymer a weight of 0.9 g.

[0062] GPC Evaluation of T1-T4 Samples: Each of T1-T4 were evaluated to determine M_w , M_n , and M_z using GPC (light scattering). The molecular weights were determined by Tosoh BioScience HLC-8320 GPC equipped with an internal differential refractive index (DRI) detector, an internal UV absorbance detector UV-8320 (254 nm absorbance Detector), a Wyatt Technology miniDawn TREOS light scattering detector with three angles (45°, 90°, and 135°), a Wyatt Technology ViscoStar-II viscometer detector, and a series of three of Polymer Labs PLgel Mixed-B with peak M_w range of 580-10,000,000. The columns were calibrated using Polymer Labs EasiVial polystyrene standards (high, medium, and low). Approximately 20 mg of polymer was dissolved in 10 mL of tetrahydrofuran (THF) stabilized with butylated hydroxyl toluene (BHT) and with toluene as a flow marker, the solution was filtered by using a 0.45 μm Acrodisc filter (membrane type polytetrafluoroethylene (PTFE)), and 150 μL samples were injected by an auto injector. Testing conditions included: sample solvent of THF containing 250-400 ppm of BHT, sample concentration of 2.0 mg/mL; sample dissolution temperature of about 23°C; sample dissolution time of 3 hours minimum on a dissolving wheel; GPC pump oven and column oven temperatures of 40°C; flow rate of 1 mL/min; mobile phase solvent of THF (same as sample solvent); sample injection size of 150 μL ; and sample elution time of 65 minutes. Wyatt Technology's Astra 6.1 Gel Permeation Chromatography Software was used for data analysis. Universal calibration curve methodology data was primarily used for reporting the results. For detailed understanding of the molecular weights of

the elastomers, on-line light scattering measurements, using a laser light scattering (LLS) detector connected on-line with the columns and other detectors were used. Samples for light scattering were prepared with care to avoid the presence of particulate matter. The Wyatt Technology's Astra 6.1 Gel Permeation Chromatography Software was used for data analysis. The results are shown in Table 2 below and FIG. 1 shows the GPC curve for T1, including extrapolation for both directions and regression line with fit adjusted to $R^2=1.0000$:

TABLE 2

Sample	Mw (kDa)	Mn (kDa)	Mz (kDa)
T1	136.2	103.3	174.7
T2	658.8	405.0	2145.0
T3	101.9	91.8	116.9
T4	98.5	47.9	200.4

- 10 **[0063]** As shown, each of T1-T2 demonstrate suitable high molecular weights (compared to most conventional cationic catalyst systems for polymerization of norbornene). Noticeably, the T2 sample comprising MeCl exhibits the greatest Mw, Mn, and Mz values, whereas the T4 sample comprises MeCl with a comparatively double amount of $(\text{CH}_3)_3\text{Si-Cl}$ catalyst and $\text{C}_{24}\text{BF}_{20}\text{Li} \cdot 2.5\text{C}_4\text{H}_{10}\text{O}$ co-catalyst but exhibits much lower Mw, Mn, and Mz values. The same is true of the T1 sample compared to the T3 sample, the T3 sample having comparatively double amount of $(\text{CH}_3)_3\text{Si-Cl}$ catalyst and $\text{C}_{24}\text{BF}_{20}\text{Li} \cdot 2.5\text{C}_4\text{H}_{10}\text{O}$ co-catalyst.

DSC Evaluation of T1-T2 Samples: Each of T1-T4 were evaluated to determine Tg using DSC. The results are shown in Table 3 below and FIGS. 2A-2D shows the DSC curves of samples T1-T4, respectively:

TABLE 2

Sample	Tg (°C)
T1	173.5
T2	181.8
T3	177.6
T4	185.4

[0064] As shown, the T1-T4 samples demonstrate suitable T_g values and are generally comparable. The T2 and T4 samples comprising MeCl solvent showed slightly higher T_g values.

[0065] Mechanical Properties of T1 and T2 Samples: Each of T1 and T2 were evaluated to determine the mechanical properties of T1 and T2 samples, per the ASTM described above. The samples were prepared per ISO 37, in which T1 and T2 samples were prepared by compression molding on a WABASH press (with controlled cooling) at 190°C-220°C, the tensile mold designed for Type 2 bars. The samples were pre-heated (at contact pressure) for 3 minutes, at low pressure for three minutes, and at high pressure for three minutes. Thereafter, the samples were control-cooled at a rate of 15°C per minute to RT and used for physical properties testing. The results are shown in Table 3 below:

TABLE 3

Test	Sample	
	T1	T2
Young's Modulus (MPa)	2313	2255
Tensile Strength at Maximum Load (MPa)	23.3	19.7
Strain at Break (%)	1.1	1.2

[0066] The T1 and T2 samples were observed to be optically clear (as were the T3 and T4 samples described above, but not mechanically tested here) and further, as shown, the T1 and T2 samples both demonstrate comparable and suitable mechanical properties for producing quality, tough materials (products) therefrom.

[0067] EXAMPLE 2: In this Example, cationic polymerization according to the present disclosure was carried out in the presence of a polar solvent of hexane alone (comparative) or a combination of polar solvents hexane and MeCl. Two separate samples (T5 and T6) were prepared comprising the below compositions provided in Table 4:

TABLE 4

Component	Sample	
	T5	T6
Norbornene Monomers (mL)	30.0	30.0
(CH ₃) ₃ Si-Cl Catalyst (μL)	12.8	12.8
C ₂₄ BF ₂₀ Li · 2.5C ₄ H ₁₀ O Co-Catalyst (mL)	10.0	10.0
MeCl Solvent (mL)	25.0	0.0
Hexane Solvent (mL)	25.0	50.0
Toluene (mL)	5.0	5.0
Polymerization Conversion (%)	6.8	12.9

[0068] T5 Polymerization Parameters: Polymerization was performed in a three-neck flask in a cold bath at -41°C, which was pre-weighed and had a weight of 2.7 g. The (CH₃)₃Si-Cl catalyst, C₂₄BF₂₀Li · 2.5C₄H₁₀O co-catalyst, the hexane polar solvent, the MeCl polar solvent, and the toluene solvent was added to the tube. Thereafter, the norbornene monomers were added to the tube for a reaction time of about 30 min at -41°C. With reference to Table 4 and the method of catalyst mixture, the catalyst mixture included 12.8μl (CH₃)₃Si-Cl catalyst with 0.7 mL of 0.15M C₂₄BF₂₀Li · 2.5C₄H₁₀O co-catalyst in 10 mL toluene (as a solvent for catalyst preparation), added slowly using a dripping funnel to the ENB dissolved in the solvent or solvent mixture. After, the polymerization was ceased by the addition of IPA. The precipitated polymer was separated, re-dissolved, dried, and tested as described below. The weight of the recovered polymer in combination with the test tube weight was 4.5 g, giving the recovered polymer a weight of 1.8 g.

[0069] T6 Polymerization Parameters: Polymerization was performed in a three-neck flask in a cold bath at -41°C, which was pre-weighed and had a weight of 2.7 g. The (CH₃)₃Si-Cl catalyst, C₂₄BF₂₀Li · 2.5C₄H₁₀O co-catalyst, the hexane (only) polar solvent, and the toluene was added to the tube. Thereafter, the norbornene monomers were added to the tube for a reaction time of about 30 min at -41°C. With reference to Table 4 and the method of catalyst mixture, the catalyst mixture included 12.8μl (CH₃)₃Si-Cl catalyst with 0.67 mL of 0.15M C₂₄BF₂₀Li · 2.5C₄H₁₀O co-catalyst in

10 mL toluene (as a solvent for catalyst preparation), added slowly using a dripping funnel to the ENB dissolved in the solvent or solvent mixture. After, the polymerization was ceased by the addition of IPA. The precipitated polymer was separated, re-dissolved, dried, and tested as described below. The weight of the recovered polymer in combination with the test tube weight was 6.1 g, giving the recovered polymer a weight of 3.4 g.

[0070] GPC Evaluation of T5 and T6 Samples: Each of T5 and T6 were evaluated to determine Mw, Mn, and Mz using GPC (light scattering). The results are shown in Table 5 below:

TABLE 5

Sample	Mw (kDa)	Mn (kDa)	Mz (kDa)
T5	16.2	77.2	262.3
T6	77.1	220.7	496.5

[0071] As shown, the sample comprising the MeCl and hexane polar solvent combination (T6) exhibits greater Mw, Mn, and Mz values compared to the hexane polar solvent alone (T5), but are less compared to the T2 sample above. The mixture of the MeCl and hexane polar solvents nevertheless exhibit suitable Mw, Mn, and Mz values as described herein.

[0072] DSC Evaluation of T5 and T6 Samples: Each of T5 and T6 were evaluated to determine Tg using DSC. The results are shown in Table 6 below:

TABLE 6

Sample	Tg (°C)
T5	178.3°C
T6	190.1°C

[0073] As shown, the T5 and T6 samples demonstrate suitable Tg values and are generally comparable. The T6 sample comprising MeCl polar solvent showed slightly higher Tg value, and further no gel formation was observed.

[0074] Nuclear Magnetic Resonance Spectroscopy (NMR) of T5 and T6 Samples: ¹H NMR spectra of T5 and T6 was obtained using an Agilent DD2 500MHz spectrometer with a 5mm H/F probe at 25°C. A tip angle of 30° was used with a 5 second delay and 128 transients using standard 5 mm tubes at room temperature. T5 and T6 Samples were dissolved at a concentration of 30mg/mL in CDCl₃. Assignments and calculations for olefinic proton content (mol%) were based on Bermeshev et.al. Macromolecules, 2014, 47, 5470-5483. The results are shown in Table 7 below:

TABLE 6

Sample	Olefinic Proton Content
T5	1.9 mol%
T6	2.5 mol%

[0075] As shown, the T6 sample comprising MeCl polar solvent showed a higher olefinic proton content compared to the T5 sample with only hexane polar solvent.

5 [0076] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular examples and configurations disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as
10 described in the claims below. It is therefore evident that the particular illustrative examples disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of “comprising,”
15 “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently,
20 “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

CLAIMS

The invention claimed is:

1. A cationic polymerization method comprising:
reacting, under reaction conditions:
5-Ethylidene-2-norbornene (ENB) monomers;
a catalyst trimethylsilylchloride;
a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and
an optional polar solvent,
thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB).
2. The cationic polymerization method of claim 1, wherein the reaction conditions comprise a reaction temperature in the range of about 20°C to about -45°C.
3. The cationic polymerization method of claim 1, wherein the reaction conditions comprise a reaction time in the range of about 10 minutes to about 90 minutes.
4. The cationic polymerization method of claim 1, further comprising initially reacting the ENB monomers and the trimethylsilylchloride catalyst under the reaction conditions for about 1 minute.
5. The cationic polymerization method of claim 1, wherein the polar solvent is present and selected from the group consisting of methyl chloride, hexane, and any combination thereof.
6. The cationic polymerization method of claim 1, wherein the polar solvent is present and is methyl chloride.
7. The cationic polymerization method of claim 1, wherein the polyENB has a weight average molecular weight in the range of about 50 kilodaltons to about 700 kilodaltons.
8. The cationic polymerization method of claim 1, wherein the polyENB has a glass transition temperature in the range of about 100°C to about 250°C.

9. The cationic polymerization method of claim 1, wherein the polyENB has a tensile strength in the range of about 15 megapascals to about 30 megapascals.
10. The cationic polymerization method of claim 1, wherein the polyENB has a Young's Modulus in the range of about 2,000 megapascals to about 3,000 megapascals.
11. The cationic polymerization method of claim 1, wherein the polyENB has a strain at break in the range of about 1% to about 5%.
12. A composition comprising:
a catalytic polymerization reaction product of:
5-Ethylidene-2-norbornene (ENB) monomers;
a catalyst trimethylsilylchloride;
a co-catalyst of lithium tetrakis(pentafluorophenyl) borate ethyl etherate; and
an optional polar solvent,
thereby producing a 5-Ethylidene-2-norbornene polymer (polyENB).
13. The composition of claim 12, wherein the polar solvent is present and selected from the group consisting of methyl chloride, hexane, and any combination thereof.
14. The composition of claim 12, wherein the polar solvent is present and is methyl chloride.
15. The composition of claim 12, wherein the ENB monomers and the trimethylsilylchloride catalyst are present in a ratio of about 400:1 to about 5000:1.
16. The composition of claim 12, wherein the polyENB has a weight average molecular weight in the range of about 50 kilodaltons to about 700 kilodaltons.
17. The composition of claim 12, wherein the polyENB has a glass transition temperature in the range of about 100°C to about 250°C.

18. The composition of claim 12, wherein the polyENB has a tensile strength in the range of about 15 megapascals to about 30 megapascals.
19. The composition of claim 12, wherein the polyENB has a Young's Modulus in the range of about 2,000 megapascals to about 3,000 megapascals.
20. The composition of claim 12, wherein the polyENB has a strain at break in the range of about 1% to about 5%.
21. The composition of claim 12, wherein the polyENB has an olefinic proton content of less than about 5 mol%