

MULTI STAGE PROCESS FOR PRODUCING ETHYLENE-BASED POLYMER WITH (ULTRA) HIGH MOLECULAR WEIGHT POLYETHYLENE COMPONENT**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/510,435 filed June 27, 2023, the entire disclosure of which is hereby incorporated herein by reference.

TECHNICAL FIELD

[0002] The present specification generally relates to processes of making ethylene-based polymers, and in particular, methods of making ethylene based polymer comprising an ultrahigh molecular weight component.

BACKGROUND

[0003] To improve toughness and processability of ethylene-based polymer (e.g., LLDPE), (ultra) high molecular weight polyethylene (UHMWPE) material may be added to ethylene-based polymer. Currently, UHMWPE is produced using heterogenous catalysts, in slurry phase or gas phase. Adding UHMWPE conventionally via blending results in relatively large UHMWPE particles, consisting of highly entangled macromolecules. Incorporation of these entangled clusters of UHMWPE in the molecular structure of an ethylene-based polymer is difficult because of the extreme viscosity differences. Specifically, the UHMWPE may have a melt index (I_2) of less than 0.01, whereas the bulk resin (e.g., LLDPE) may have a melt index at least a hundred times greater than that. Thus, there is a continual need for processes to better incorporate UHMWPE into ethylene-based polymers, such as LLDPE.

SUMMARY

[0004] Embodiments of the present disclosure meet this need for improved UHMWPE incorporation by producing UHMWPE in solution at low to moderate reaction temperatures, wherein the catalyst used is not for particle formation (as in slurry or gas phase technology), but aims at producing UHMWPE chains which are evenly dispersed either dissolved or as fine mist (very fine phase separated) in the solvent. In the subsequent solution process conditions, the dissolved or dispersed UHMWPE will be solution blended with the ethylene-based polymer. This

results in a highly dis-entangled UHMWPE fraction in solution, which is easily incorporated in the downstream solution reactor used to produce the ethylene-based polymer.

[0005] According to one embodiment, a method of producing ethylene-based polymer comprising first and second polymer fractions is provided. The method comprising reacting ethylene monomer and optionally C₃-C₁₂ α -olefin comonomer in solvent in the presence of a reaction A catalyst in at least one tubular reactor to produce the first polymer fraction reaching an exit temperature of this reaction zone below 160 °C, wherein the weight averaged molecular weight (Mw) of this first polymer fraction is larger than 500,000 g/mol; introducing the first polymer fraction, ethylene monomer, C₃-C₁₂ α -olefin comonomer, solvent, at least two reaction B catalysts, and a shuttling agent to at least one agitated solution polymerization reactor; reacting the ethylene monomer and C₃-C₁₂ α -olefin comonomer in solvent in the presence of the at least two reaction B catalysts and the shuttling agent in the at least one agitated solution polymerization reactor to produce a second polymer fraction; and outputting effluent from the agitated solution polymerization reactor, wherein the effluent comprises the ethylene-based polymer having the first and second polymer fractions, unreacted ethylene monomer, and optionally unreacted C₃-C₁₂ α -olefin comonomer, wherein the ethylene-based polymer comprises 0.1 to 15 wt.% of the first polymer fraction and more than 70 wt.% of the second polymer fraction, and wherein the ethylene-based polymer has a melt index (I₂) from 0.2 g/10 mins to 20 g/10 mins., a density between 0.880 g/cc to 0.908 g/cc and has an Mz/Mw greater than the Mw/Mn.

[0006] According to one embodiment, an elastic article may comprise a polymer having a melt index (I₂) from 0.2 g/10 mins to 20 g/10 mins., a density between 0.880 g/cc to 0.908 g/cc and Mz/Mw greater than the Mw/Mn, wherein the polymer has been oriented to at least 4 times its original dimensions.

[0007] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the drawings, the detailed description which follows and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 is a schematic view of the present process according to one or more embodiments of the present disclosure;

[0009] FIG. 2 is another schematic view of the present process according to one or more embodiments of the present disclosure; and

[0010] FIG. 3 is yet another schematic view of the present process according to one or more embodiments of the present disclosure.

DETAILED DESCRIPTION

[0011] Specific embodiments of the present application will now be described. The disclosure may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth in this disclosure. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

DEFINITIONS

[0012] The term "polymer" refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term "homopolymer," usually employed to refer to polymers prepared from only one type of monomer as well as "copolymer" which refers to polymers prepared from two or more different monomers. The term "interpolymer," as used herein, refers to a polymer prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers, and polymers prepared from more than two different types of monomers, such as terpolymers.

[0013] "Polyethylene" or "ethylene based polymer" shall mean polymers comprising greater than 50% by weight of units which have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more comonomers). Comonomers may include olefin comonomers as well as polar comonomers. Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE);

Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); single-site catalyzed Linear Low Density Polyethylene, including both linear and substantially linear low density resins (m-LLDPE); Medium Density Polyethylene (MDPE); and High Density Polyethylene (HDPE).

[0014] The term "LDPE" may also be referred to as "high pressure ethylene polymer" or "highly branched polyethylene" and is defined to mean that the polymer is partly or entirely homopolymerized or copolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators, such as peroxides (see for example US 4,599,392, which is hereby incorporated by reference). LDPE resins typically have a density in the range of 0.916 grams per cubic centimeter (g/cc) to 0.935 g/cc.

[0015] The term "LLDPE", includes resin made using Ziegler-Natta catalyst systems as well as resin made using single-site catalysts, including, but not limited to, bis-metallocene catalysts (sometimes referred to as "m-LLDPE") and constrained geometry catalysts, and resin made using post-metallocene, molecular catalysts. LLDPE includes linear, substantially linear or heterogeneous polyethylene copolymers or homopolymers. LLDPEs contain less long chain branching than LDPEs and includes the substantially linear ethylene polymers which are further defined in U.S. Patent 5,272,236, U.S. Patent 5,278,272, U.S. Patent 5,582,923 and US Patent 5,733,155; the homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992; the heterogeneously branched ethylene polymers such as those prepared according to the process disclosed in U.S. Patent No. 4,076,698; and/or blends thereof (such as those disclosed in US 3,914,342 or US 5,854,045). The LLDPE resins can be made via gas-phase, solution-phase or slurry polymerization or any combination thereof, using any type of reactor or reactor configuration known in the art.

[0016] The term "MDPE" refers to polyethylenes having densities from 0.926 to 0.940 g/cc. "MDPE" is typically made using chromium or Ziegler-Natta catalysts or using single-site catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts.

[0017] The term "HDPE" refers to polyethylenes having densities greater than about 0.940 g/cc, which are generally prepared with Ziegler-Natta catalysts, chrome catalysts or single-site catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts.

[0018] The term “UHMWPE” refers to polyethylenes having weight average molecular weight (Mw) greater than 500,000 g/mol as measured according to conventional Gel Permeation Chromatography.

[0019] The term “disentangled network” refers to a polymer wherein the chains are less interconnected, thereby allowing increased flow, processability, and drawability. In contrast, the term “entangled network” refers to highly to a polymer wherein the chains are highly interconnected, thereby reducing flow, processability, and drawability.

[0020] As used herein “Mn” refers to the number averaged molecular weight of a polymer. As used herein “Mw” refers to the weight averaged molecular weight of a polymer. As used herein “Mz” refers to the Z-averaged molecular weight of a polymer, where z stands for centrifugation. Unless otherwise indicated, Mn, Mw, and Mz are each given in units of grams per mol (g/mol).

[0021] As used herein “Dwn” refers to Mw/Mn.

[0022] As used herein “Dzn” refers to Mz/Mn.

[0023] As used in the present disclosure, the terms “blend” or “polymer blend,” as used, refer to a mixture of two or more polymers. A blend may or may not be miscible (phase separated at the molecular level). A blend may or may not be phase separated. A blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art. The blend may be prepared by physically mixing the two or more polymers on the macro level (for example, melt blending resins or compounding) or the micro level (for example, simultaneous forming within the same reactor). It is possible to prepare the blends in a melt phase or using solution blending in a common solvent.

[0024] The terms “comprising,” “including,” “having,” and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term “comprising” may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of any succeeding recitation any other component, step or procedure,

excepting those that are not essential to operability. The term “consisting of” excludes any component, step or procedure not specifically delineated or listed.

[0025] Embodiments of the present disclosure are directed to systems and methods for producing ethylene-based polymer comprising first and second polymer fractions. The first polymer fraction may also be referred to herein as the high molecular weight fraction or the “HMW fraction”, whereas the second polymer fraction may also be referred to herein as the “bulk fraction.” Referring to FIGS. 1 and 3, the method may comprise reacting ethylene monomer and C₃-C₁₂ α -olefin comonomer in solvent 10 in the presence of a reaction A catalyst 20 in at least one tubular reactor 100 to produce a first polymer fraction 130 reaching an exit temperature of this reaction zone below 160 °C, wherein the weight averaged molecular weight (Mw) of this first polymer fraction is larger than 500,000 g/mol. The first polymer fraction may also be considered the UHMWPE fraction. Various means for supplying the monomer, solvent and catalyst are considered suitable. In another embodiment, as shown in FIG. 2, ethylene 2, C₃-C₁₂ α -olefin comonomer 4, and solvent 6 may mix in a mixing vessel 50 upstream of the at least one tubular reactor 100. While FIG. 2 depicts the mixing vessel 50 as a continuous stirred tank reactor (CSTR), various additional mixing containers are considered suitable. Further, as shown in FIG. 2, the procatalyst 22 and cocatalyst 24 may be fed separately as shown, or alternatively as shown in FIG. 1 catalyst may be fed in a single stream 20.

[0026] In one or more embodiments, the at least one

[0027] tubular reactor 100 may comprise a plug flow reactor. Moreover, as stated above, the exit temperature may be less than 160 °C, less than 157 °C, less than 155 °C, or less than 150 °C. Further, the exit temperature may be from 60 °C to 160 °C, from 60 °C to 155 °C, from 60 °C to 150 °C, from 60 °C to 90 °C, 100 °C to 160 °C, from 100 °C to 155 °C, from 100 °C to 150 °C, 120 °C to 160 °C, from 120 °C to 155 °C, from 120 °C to 150 °C, or from 80 °C to 110 °C, or from or from 120 °C to 160 °C, or from 120 °C to 145 °C or from 130 °C to 155 °C, 140 °C to 160 °C, or from 30 °C to 160 °C, or from 30 °C to 155 °C, or from 30 °C to 150 °C. Pressures may range from about 400 psi to about 1000 psi, or from about 650 psi to about 800 psi. The residence time may be from about 0.5 minutes to about 15 minutes, or from about 0.5 minutes to about 2 minutes. In other embodiment, the tubular reactor may be operated at adiabatic conditions. In other embodiment, the tubular reactor may be operated with cooling, heating, or a combination.

[0028] Various solvents are considered suitable. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR E (ExxonMobil Chemical Co., Houston, Tex.).

[0029] Within the first fraction, the ethylene monomer may be present in an amount of at least 50 wt.%, or at least 60 wt.%, or at least 70 wt.%, or at least 80 wt.%.

[0030] In embodiments, the C₃-C₁₂ α -olefin comonomer may comprise one or more of octene, hexene, or 4-methyl-1-pentene. The C₃-C₁₂ α -olefin comonomer may be present in the first fraction at an amount of at less than 50 wt.%, or less than 40 wt.%, or less than 30 wt.%, or less than 20 wt.%. It should be understood that the amount of comonomer used will help to control the density range of the first fraction. In embodiments, the C₃-C₁₂ α -olefin comonomer may be present in the first fraction at an amount of from 2 wt. % to 20 wt. %, on the basis of the total polymer weight of the first fraction.

[0031] The reaction A catalyst may comprise at least one molecular catalyst, at least one heterogeneous Ziegler-Natta catalyst, or combinations thereof. Constrained geometry and metallocene catalysts are also contemplated as suitable. In one embodiment, the reaction A catalyst comprises a molecular catalyst. The molecular catalyst may comprise one or more bis-biphenyl-phenoxy catalysts. Without being bound by theory, using a molecular homogeneous catalyst in a temperature regime less than 160 °C helps create a UHMWPE first fraction in a phase separated mode which can be better incorporated into the second polymer fraction produced in the downstream agitated solution polymerization reaction as defined further below. Further without being bound by theory, constrained crystallization of these UHMWPE chains gives the potential to modify performance characteristics of the overall polymer.

[0032] The first polymer fraction may have a weight averaged molecular weight (Mw) greater than 500,000 g/mol, greater than 750,000 g/mol, or greater than 1,000,000 g/mol as measured according to gel permeation chromatography. Additionally, the first polymer fraction may comprise an Mw from 500,000 to 1,500,000 g/mol, from 500,000 to 1,250,000 g/mol, from 500,000 to 1,100,000 g/mol, from 750,000 to 1,500,000 g/mol, from 750,000 to 1,250,000 g/mol, from 750,000 to 1,100,000 g/mol, from 900,000 to 1,500,000 g/mol, from 900,000 to 1,200,000 g/mol, or from 900,000 to 1,100,000 g/mol. Moreover, the first polymer fraction may comprise a number averaged molecular weight (Mn) greater than 350,000 g/mol, or greater than 400,000

g/mol, or greater than 500,000 g/mol as measured according to gel permeation chromatography. Additionally, the first polymer fraction may comprise an Mn from 350,000 to 750,000 g/mol, from 350,000 to 600,000 g/mol, from 400,000 to 750,000 g/mol, or from 400,000 to 600,000 g/mol. Furthermore, the first polymer fraction may have an MWD ($=M_w/M_n$) from 1 to 5, from 1 to 4, from 3 to 5, or from 1 to 3.

[0033] Moreover, the density of the first polymer fraction may range from 0.870 to 0.920 g/cc, from 0.870 to 0.900 g/cc, from 0.870 to 0.890 g/cc, 0.880 to 0.920 g/cc, from 0.880 to 0.900 g/cc, from 0.880 to 0.890 g/cc, 0.890 to 0.920 g/cc, from 0.890 to 0.900 g/cc, from 0.900 to 0.920 g/cc, or any subset thereof. The melt index (I_2) may range from 0.00001 to 0.5 dg/min, from 0.0001 to 0.1 dg/min, or 0.0001 to 0.05 dg/min.

[0034] In embodiments, the first polymer fraction may have a short chain branching distribution (SCBD) melting temperature of from 50 °C to 90 °C, such as from 60 °C to 90 °C, from 70 °C to 90 °C, from 50 °C to 80 °C, from 50 °C to 70 °C, from 60 °C to 80 °C, or any subset thereof. The SCBD melting temperature may be determined through deconvolution of the improved comonomer content distribution (iCCD) analysis.

[0035] Referring to FIGS. 1-3, the first polymer fraction 130, ethylene monomer 110, C₃-C₁₂ α -olefin comonomer 120, solvent, at least two reaction B catalysts, and a shuttling agent 140 may be fed to at least one agitated solution polymerization reactor 200 to effectuate a reaction B. In the at least one agitated solution polymerization reactor 200, the ethylene monomer and optionally C₃-C₁₂ α -olefin comonomer react in solvent in the presence of the at least two reaction B catalysts and the shuttling agent (also referred to herein as the “reaction B catalyst system”) to produce a second polymer fraction. The at least two reaction B catalysts and the shuttling agent may be referred to as the reaction B catalyst system.

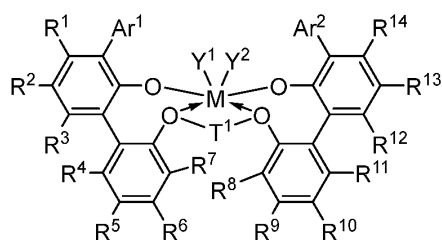
[0036] In one or more embodiments, the at least one agitated solution polymerization reactor 200 may comprise at least one continuous stirred tank reactor (CSTR), at least one loop reactor, or combinations thereof. Moreover, as stated above, the exit temperature may be greater than 150 °C, such as greater than 155 °C, greater than 160 °C, from 150 °C to 205 °C, from 155 °C to 205 °C, from 160 °C to 205 °C, or any subset thereof. Pressures may range from about 30 psi (2 bar) to about 1000 psi (68.9 bar), or from about 30 psi (2 bar) to about 750 psi (51.7 bar). The residence time may be from about 2 to about 20 minutes, or from about 10 to about 20 minutes. In an

additional embodiment, the CSTR or Loop Reactor exit is connected to another tubular post reactor, which may reach an exit temperature above 205 °C.

[0037] Like the upstream tubular reactor, various solvents are considered suitable. Exemplary solvents include, but are not limited to, isoparaffins, such as ISOPAR E. In one or more embodiments, the fraction of first polymer in the at least one agitated solution polymerization reactor 200 may be less than 5 wt.%, less than 2 wt.%, less than 1 wt.%.

[0038] Within the second polymer fraction, the ethylene monomer may be present in an amount of at least 50 wt.%, or at least 60 wt.%, or at least 70 wt.%, or at least 80 wt.%. Conversely, the C₃-C₁₂ α -olefin comonomer may be present in the second fraction at an amount of at less than 50 wt.%, or less than 40 wt.%, or less than 30 wt.%, or less than 20 wt.%. The C₃-C₁₂ α -olefin comonomer may be octene. It should be understood that the amount of comonomer used will help to control the density range of the second polymer fraction.

[0039] Referring again to the reaction B catalyst system, various compositions are considered suitable for the at least two reaction B catalysts and the chain transfer agent. The reaction B catalyst system may include (i) a first reaction B polymerization catalyst and (ii) a second reaction B polymerization catalyst, and (iii) a chain shuttling agent. The first reaction B polymerization catalyst may have the structure of Formula (I)



Formula (I)

wherein

M may be titanium, zirconium, or hafnium;

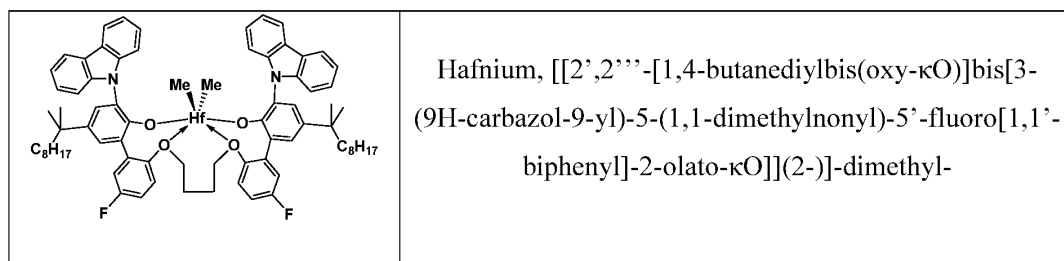
each Y¹ and Y² may be independently selected from the group consisting of (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)trihydrocarbylsilylhydrocarbyl, halogen, alkoxide, or amine, or two Y groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group;

each Ar¹ and Ar² independently may be selected from the group consisting of (C₆-C₄₀)aryl, substituted (C₆-C₄₀)aryl, (C₃-C₄₀)heteroaryl, and substituted (C₃-C₄₀)heteroaryl;

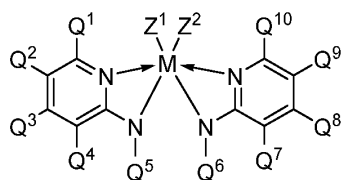
T¹ independently at each occurrence may be a saturated C₂-C₄ alkyl that forms a bridge between the two oxygen atoms to which T¹ is bonded; and

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, and R¹⁴ independently may be selected from the group consisting of hydrogen, a halogen, (C₁-C₄₀)hydrocarbyl, substituted (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, substituted (C₁-C₄₀)heterohydrocarbyl, (C₆-C₄₀)aryl, substituted (C₆-C₄₀)aryl, (C₃-C₄₀)heteroaryl, and substituted (C₃-C₄₀)heteroaryl, and nitro (NO₂).

[0040] In embodiments, the first reaction B polymerization catalyst may be



[0041] The second reaction B polymerization catalyst may have the structure of Formula (II)



Formula (II)

wherein

M may be titanium, zirconium, or hafnium,

each Z¹ and Z² may be independently selected from the group consisting of (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)trihydrocarbylsilylhydrocarbyl, halogen, alkoxide, or amine, or two Z groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group;

each Q¹ and Q¹⁰ independently may be selected from the group consisting of (C₆-C₄₀)aryl, substituted (C₆-C₄₀)aryl, (C₃-C₄₀)heteroaryl, and substituted (C₃-C₄₀)heteroaryl;

each Q², Q³, Q⁴, Q⁷, Q⁸, and Q⁹ independently may be selected from the group consisting of hydrogen, (C₁-C₄₀)hydrocarbyl, substituted (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, substituted (C₁-C₄₀)heterohydrocarbyl, halogen, and nitro (NO₂);

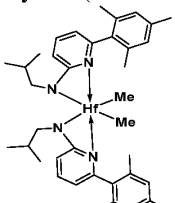
each Q^5 and Q^6 independently may be selected from the group consisting of (C₁-C₄₀)alkyl, substituted (C₁-C₄₀)alkyl, and [(Si)₁-(C+Si)₄₀] substituted organosilyl;

each N independently is nitrogen;

optionally, two or more of the Q^{1-5} groups combine together to form a ring structure, with such ring structure having from 5 to 16 atoms in the ring excluding any hydrogen atoms; and

optionally, two or more of the Q^{6-10} groups can combine together to form a ring structure, with such ring structure having from 5 to 16 atoms in the ring excluding any hydrogen atoms.

[0042] In embodiments, the second reaction B polymerization catalyst may be

Catalyst 2 (secondary) 	Hafnium, dimethylbis[N-(2-methylpropyl)-6-(2,4,6-trimethylphenyl)-2-pyridinaminato-κN1, κN2]-
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[0043] The catalyst system may also include a chain shuttling agent. A "chain shuttling agent," as used herein, refers to a compound that is capable of causing polymeryl transfer between various active catalyst sites under the polymerization conditions. That is, transfer of a polymer fragment occurs both to and from an active catalyst site in a facile and reversible manner. In contrast to a shuttling agent or chain shuttling agent, an agent that acts merely as a "chain transfer agent," such as some main-group alkyl compounds, may exchange, for example, an alkyl group on the chain transfer agent with the growing polymer chain on the catalyst, which generally results in termination of the polymer chain growth. In this event, the main-group center may act as a repository for a dead polymer chain, rather than engaging in reversible transfer with a catalyst site in the manner in which a chain shuttling agent does. Desirably, the intermediate formed between the chain shuttling agent and the polymeryl chain is not sufficiently stable relative to exchange between this intermediate and any other growing polymeryl chain, such that chain termination is relatively rare. Chain shuttling agents and the chain shuttling process are described in U.S. Patent 7,858,706, which is herein incorporated by reference. In embodiments, the chain shuttling agent may comprise diethyl zinc.

[0044] The ethylene monomer and C₃-C₁₂ α -olefin comonomer may have a residence time R₁ in the at least one tubular reactor. The ethylene monomer and optionally C₃-C₁₂ α -olefin comonomer may have a residence time R₂ in the at least one agitated solution polymerization reactor. A ratio of R₁/R₂ may be from 0.1 to 0.5, such as from 0.1 to 0.4, from 0.1 to 0.3, from 0.1 to 0.2, from 0.125 to 0.5, from 0.125 to 0.4, from 0.125 to 0.3, from 0.125 to 0.2, from 0.2 to 0.5, from 0.3 to 0.4, or any subset thereof. Without being limited by theory, it is believed that the ratio of the residence time in the tubular reactor to the residence time in the agitated solution polymerization reactor may help to control the ratio of high molecular weight polymer to low molecular weight polymer.

[0045] In one or more embodiments, the second polymer fraction comprises a multi-block copolymer, such as an ethylene-octene multi-block copolymer. The multi-block copolymer typically contains high-density “hard” segments and low-density “soft” segments. This multi-block copolymer provides the benefits of both the durability and high temperature resistance of high-density polyethylene while maintaining key properties of elastomeric, low-density polyolefin such as elastic behavior, flexibility, and processability. The term “multi-block copolymer” is a copolymer consisting of ethylene and comonomer in polymerized form, the polymer characterized by multiple blocks or segments of two polymerized monomer units (*i.e.*, ethylene and octene) differing in chemical or physical properties, the blocks joined (or covalently bonded) in a linear manner, that is, a polymer comprising chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality. The multi-block copolymer includes block copolymer with two blocks (di-block) and more than two blocks (multi-block). The multi-block copolymer is void of, or otherwise excludes, styrene (*i.e.*, is styrene-free), and/or vinyl aromatic monomer, and/or conjugated diene. When referring to amounts of “ethylene” or “comonomer” in the copolymer, it is understood that this refers to polymerized units thereof. The ethylene/octene multi-block copolymer can be represented by the following formula: (AB)_n; where n is at least 1, preferably an integer greater than 1, such as 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, or higher, “A” represents a hard block or segment, and “B” represents a soft block or segment. The As and Bs are linked, or covalently bonded, in a substantially linear fashion, or in a linear manner, as opposed to a substantially branched or substantially star-shaped fashion. In other embodiments, A blocks and B blocks are randomly distributed along the polymer chain. In other words, the block copolymers usually do not have a structure as follows: AAA-AA-BBB-BB. In

an embodiment, the ethylene/octene multi-block copolymer does not have a third type of block, which comprises different comonomer(s). In another embodiment, each of block A and block B has monomers or comonomers substantially randomly distributed within the block. In other words, neither block A nor block B comprises two or more sub-segments (or sub-blocks) of distinct composition, such as a tip segment, which has a substantially different composition than the rest of the block.

[0046] Ethylene may comprise the majority mole fraction of the whole multi-block copolymer. Ethylene may comprise at least 50 mole % (mol%) of the whole multi-block copolymer. In an embodiment, the multi-block copolymer contains from 50 mol%, or 60 mol %, or 65 mol % to 80 mol %, or 85 mol %, or 90 mol %, or 95 mol % ethylene and a reciprocal amount of comonomer (such as octene), or from 5 mol %, or 10 mol %, or 15 mol %, or 20 mol % to 35 mol %, or 40 mol%, or less than 50 mol% comonomer based on the total moles of the multi-block copolymer. In a further embodiment, the multi-block copolymer contains from 5 mol% to 30 mol% comonomer (and 95 mol% to 70 mol% ethylene), or from 10 mol% to 25 mol% octene (and from 90 mol% to 75 mol% ethylene).

[0047] The multi-block copolymer may comprise two or more chemically distinct regions or segments (referred to as “blocks”) joined (or covalently bonded) in a linear manner, that is, it contains chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion. The blocks differ in the amount or type of incorporated comonomer, density, amount of crystallinity, crystallite size attributable to a polymer of such composition, type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, amount of branching (including long chain branching or hyper-branching), homogeneity or any other chemical or physical property. Compared to block interpolymers of the prior art, including interpolymers produced by sequential monomer addition, fluxional catalysts, or anionic polymerization techniques, the present multi-block copolymer may be characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn or MWD), polydisperse block length distribution, and/or polydisperse block number distribution, due, in an embodiment, to the effect of the shuttling agent(s) in combination with multiple catalysts used in their preparation.

[0048] The multi-block copolymer may include various amounts of “hard” segments and “soft” segments. “Hard” segments are blocks of polymerized units in which ethylene is present in an amount greater than 90 wt.%, or 95 wt.%, or greater than 95 wt.%, or greater than 98 wt.%, based on the weight of the polymer, up to 100 wt.%. In other words, the comonomer content (content of monomers other than ethylene) in the hard segments is less than 10 wt.%, or 5 wt.%, or less than 5 wt.%, or less than 2 wt.%, based on the weight of the polymer, and can be as low as zero. In some embodiments, the hard segments include all, or substantially all, units derived from ethylene. “Soft” segments are blocks of polymerized units in which the comonomer content (such as the content of octene) is greater than 5 wt.%, or greater than 8 wt.%, or greater than 10 wt.%, or greater than 15 wt.%, based on the weight of the polymer. In an embodiment, the comonomer content in the soft segments is greater than 20 wt.%, or greater than 25 wt.%, or greater than 30 wt.%, or greater than 35 wt.%, or greater than 40 wt.%, or greater than 45 wt.%, or greater than 50 wt.%, or greater than 60 wt.% and can be up to 100 wt.%.

[0049] The soft segments can be present in the multi-block copolymer from 1 wt.%, or 5 wt.%, or 10 wt.%, or 15 wt.%, or 20 wt.%, or 25 wt.%, or 30 wt.%, or 35 wt.%, or 40 wt.%, or 45 wt.% to 55 wt.%, or 60 wt.%, or 65 wt.%, or 70 wt.%, or 75 wt.%, or 80 wt.%, or 85 wt.%, or 90 wt.%, or 95 wt.%, or 99 wt.% of the total weight of the ethylene/octene multi-block copolymer. Conversely, the hard segments can be present in similar ranges. The soft segment weight percentage and the hard segment weight percentage can be calculated based on data obtained from DSC or NMR. Such methods and calculations are disclosed in, for example, USP 7,608,668, the disclosure of which is incorporated by reference herein in its entirety. In particular, hard and soft segment weight percentages and soft segment melting temperature, SS-T_m, may be determined as described in column 57 to column 63 of USP 7,608,668, incorporated herein by reference.

[0050] The soft segments may have a soft segment melting temperature (SS-T_m) of less than 35 °C, such as from -30 °C to 35 °C, or from -30 °C to 30 °C,

[0051] In an embodiment, the multi-block copolymer is produced in a continuous process and possesses a polydispersity index (M_w/M_n) from 1.7 to 3.5, or from 1.8 to 3, or from 1.8 to 2.5, or from 1.8 to 2.2. When produced in a batch or semi-batch process, the multi-block copolymer possesses M_w/M_n from 1.0 to 3.5, or from 1.3 to 3, or from 1.4 to 2.5, or from 1.4 to 2.

[0052] In addition, the multi-block copolymer may possess a PDI (or Mw/Mn) fitting a Schultz-Flory distribution rather than a Poisson distribution. The present multi-block copolymer may have both a polydisperse block distribution as well as a polydisperse distribution of block sizes. This results in the formation of polymer products having improved and distinguishable physical properties. The theoretical benefits of a polydisperse block distribution have been previously modeled and discussed in Potemkin, *Physical Review E* (1998) 57 (6), pp. 6902–6912, and Dobrynin, *J. Chem. Phys.* (1997) 107 (21), pp. 9234–9238.

[0053] The second polymer fraction (optionally including the multi-block copolymer) may have a weight averaged molecular weight (Mw) greater than 50,000 g/mol, or greater than 75,000 g/mol, or greater than 90,000 g/mol as measured according to gel permeation chromatography. Additionally, the second polymer fraction may comprise an Mw from 50,000 to 120,000 g/mol, from 50,000 to 100,000 g/mol, from 75,000 to 120,000 g/mol, from 75,000 to 100,000 g/mol, or from 90,000 to 120,000 g/mol, from 90,000 to 100,000 g/mol. Moreover, the second polymer fraction may comprise a number averaged molecular weight (Mn) greater than 10,000 g/mol, or greater than 15,000 g/mol as measured according to gel permeation chromatography. Additionally, the second polymer fraction may comprise an Mn from 10,000 to 50,000 g/mol, from 10,000 to 25,000 g/mol, from 15,000 to 50,000 g/mol, or from 15,000 to 25,000 g/mol. Furthermore, the second polymer fraction may have an MWD (=Mw/Mn) from 1 to 5, such as from 2 to 3.

[0054] Moreover, the density of the second polymer fraction (optionally including the multi-block copolymer) may range from 0.870 to 0.940 g/cc, from 0.890 to 0.920 g/cc, or from 0.905 to 0.920 g/cc. The melt index (I₂) may range from 0.5 dg/min to 30 dg/min, from 1 dg/min to 30 dg/min, from 0.5 dg/min to 25 dg/min, from 0.5 dg/min to 20 dg/min, from 0.5 dg/min to 15 dg/min, from 0.5 dg/min to 10 dg/min, from 1 dg/min to 8 dg/min, or any subset thereof.

[0055] Referring again to FIGS. 1-3, the effluent 210 outputted from the at least one agitated solution polymerization reactor 200 may comprise the first and second polymer fractions, unreacted ethylene monomer, and optionally unreacted C₃-C₁₂ α -olefin comonomer. The ethylene-based polymer may comprise from 0.1 to 15 wt.% (such as from 0.1 to 12 wt. %, from 0.1 to 10 wt. %, from 0.1 to 8 wt. %, from 0.5 to 15 wt. %, from 0.5 to 12 wt. %, from 0.5 to 10 wt. %, from 0.5 to 8 wt. %, from 1 wt. % to 15 wt. %, from 1 wt. % to 10 wt. %, from 1 wt. % to 8 wt. %, from

2 wt. % to 15 wt. %, from 2 wt. % to 12 wt. %, from 2 wt. % to 8 wt. %, or any subset thereof) of the first polymer fraction and more than 70 wt.% of the second polymer fraction. Moreover, the ethylene-based polymer may have a melt index (I_2) from 0.2 to 20 g/10 min (such as from 0.2 to 15 g/10 min, from 0.2 to 10 g/10 min, from 0.2 to 5 g/10 min, from 0.5 to 20 g/10 min, from 0.5 to 15 g/10 min, from 0.5 to 10 g/10 min, from 0.5 to 5 g/10 min, or any subset thereof), a density between 0.870 to 0.970 g/cc and has an M_z/M_w greater than the M_w/M_n .

[0056] In embodiments, the effluent of the at least one agitated solution polymerization reactor 200 may undergo one or separation steps to isolate the ethylene based polymer from the unreacted ethylene monomer and optionally unreacted C_3 - C_{12} α -olefin comonomer.

[0057] The ethylene based polymer may comprise a weight averaged molecular weight (M_w) greater than 50,000 g/mol, greater than 50,000 g/mol, or greater than 100,000 g/mol as measured according to gel permeation chromatography. Additionally, the ethylene based polymer may comprise an M_w from 50,000 to 150,000 g/mol, from 50,000 to 120,000 g/mol, from 75,000 to 150,000 g/mol, from 75,000 to 120,000 g/mol, from 90,000 to 150,000 g/mol, or from 90,000 to 120,000 g/mol. Moreover, the ethylene based polymer may comprise a number averaged molecular weight (M_n) greater than 10,000 g/mol, or greater than 15,000 g/mol as measured according to gel permeation chromatography. Additionally, the ethylene based polymer may comprise an M_n from 10,000 to 50,000 g/mol, from 10,000 to 25,000 g/mol, from 15,000 to 50,000 g/mol, or from 15,000 to 25,000 g/mol. The ethylene based polymer may comprise a z-average molecular weight (M_z) of at least 500,000 g/mol, or 750,000 g/mol. The ethylene based polymer may comprise an M_z from 750,000 to 1,000,000 g/mol, or from 800,000 to 900,000 g/mol. Furthermore, the ethylene based polymer may have an M_z/M_w from 1 to 20, from 1 to 15, from 1 to 10, from 5 to 10, or from 5 to 7.

[0058] Moreover, the density of the ethylene based polymer may range from 0.870 to 0.940 g/cc, from 0.870 to 0.930 g/cc, from 0.870 to 0.920 g/cc, from 0.870 to 0.910 g/cc, from 0.870 to 0.910 g/cc, from 0.870 to 0.908 g/cc, from 0.880 to 0.940 g/cc, from 0.880 to 0.920 g/cc, from 0.880 to 0.908 g/cc, from 0.890 to 0.908 g/cc, from 0.900 to 0.908 g/cc, from 0.870 to 0.900 g/cc, from 0.870 to 0.890 g/cc, from 0.870 to 0.880 g/cc, or any subset thereof.

[0059] The melt index (I_2) of the ethylene based polymer may range from 0.1 to 20 g/min, from 0.5 to 20 g/10 min, from 0.5 to 15 g/10 min, from 0.5 to 10 g/10 min, from 0.5 to 5 g/10 min, from

1 to 20 g/10 min, from 5 to 20 g/10 min, from 10 to 20 g/10 min, from 15 to 20 g/10 min, from 5 to 15 g/10 min, or any subset thereof. The ethylene based polymer may have an I_{10}/I_2 from 1 to 30, from 5 to 20, from 5 to 15, from 9 to 15, or from 9 to 12.

[0060] The melt flow ratio (I_2/I_{10}) of the ethylene based polymer may be at least 9. In embodiments, the melt flow ratio of the ethylene based polymer may be at least 10, from 9 to 15, from 9 to 13, from 10 to 15, from 10 to 13, or any subset thereof.

[0061] Alternatively, as shown in FIGS. 2 and 3, the effluent 210 of the at least one agitated solution polymerization reactor 200 may be passed to a mixer 300 downstream of the at least one agitated solution polymerization reactor 200, wherein the mixer includes the addition of a reaction C catalyst 220. The reaction C catalyst facilitates further reaction of the unreacted ethylene monomer and optionally any unreacted C_3 - C_{12} α -olefin comonomer to produce a third polymer fraction having a density and a melt index (I_2) different from the second polymer fraction.

[0062] The reaction C catalyst may comprise at least one molecular catalyst, at least one heterogeneous Ziegler-Natta catalyst, or combinations thereof. Constrained geometry and metallocene catalysts are also contemplated as suitable.

[0063] In a further embodiment depicted in FIG. 3, the method comprises introducing a mixer effluent 310 from the mixer 300 to a tubular polymerization reactor 400, wherein the mixer effluent 310 comprises the ethylene-based polymer having the first, second and third polymer fractions. While the reaction C catalyst 220 may be already fed in the upstream mixer 300, it is contemplated that the reaction C catalyst or another catalyst may be added to tubular reactor 300 as shown in stream 320.

[0064] The ethylene-based polymer is considered suitable for multiple applications. For example, it is considered suitable for films (monolayer and multilayer), fibers, non-woven materials, elastic textile yarn, artificial turf and various articles incorporating these films. For example, the ethylene-based polymer may be used in a variety of films, including but not limited to, extrusion coating, food packaging, consumer, industrial, agricultural (applications or films), lamination films, fresh cut produce films, meat films, cheese films, candy films, clarity shrink films, collation shrink films, stretch films, oriented films (MDO, BOPE), silage films, greenhouse

films, fumigation films, liner films, stretch hood, heavy duty shipping sacks, pet food, sandwich bags, sealants, and diaper backsheets.

[0065] In embodiments, an elastic article may be constructed from a polymer (such as an ethylene-based polymer produced by the method of the present disclosure) having a melt index (I_2) from 0.2 g/10 mins to 20 g/10 mins., a density between 0.880 g/cc to 0.908 g/cc and has an M_z/M_w greater than the M_w/M_n .

[0066] The polymer of the elastic article may have been oriented to at least 4 times its original dimensions, such as surface area. "Orienting" a film refers to the process of stretching the in the machine direction, in the cross or transverse direction, or both to improve physical and/or barrier properties. For example, the film may be heated and biaxially stretched in the machine and cross direction over a series of rollers. As used herein, the terms "machine direction" means the length of a film in the direction in which it is produced. The terms "cross direction" or "transverse direction" or "cross directional" mean the width of film, i.e. a direction generally perpendicular to the machine direction. Biaxially oriented films may exhibit improved tensile properties as compared with those not subjected to the biaxial orientation procedure. In embodiments, the polymer of the elastic article may have been oriented to at least 6 times, at least 8 times, from 4 times to 10 times, from 4 times to 8 times, from 4 times to 6 times, or any subset thereof its original dimensions.

[0067] In embodiments, the polymer may have been allowed to relax after having been oriented.

TEST METHODS

[0068] Density

[0069] Samples for density measurement are prepared according to ASTM D 1928. Polymer samples are pressed at 190 °C and 30,000 psi for three minutes, and then at 21 °C and 207 MPa for one minute. Measurements are made within one hour of sample pressing using ASTM D792, Method B.

[0070] Melt Index (I_2)

[0071] Melt index, or I_2 , (grams/10 minutes or dg/min) is measured in accordance with ASTM D 1238, Condition 190 °C/2.16 kg, Procedure B.

[0072] Melt Index (I₁₀)

[0073] Melt index, or I₁₀, (grams/10 minutes or dg/min) is measured in accordance with ASTM D 1238, Condition 190 °C/10 kg, Procedure B.

[0074] Melt Strength

[0075] Melt strength was measured at 190 °C using a Goettfert Rheotens 71.97 (Goettfert Inc.; Rock Hill, S.C.), melt fed with a Goettfert Rheotester 2000 capillary rheometer equipped with a flat entrance angle (180 degrees) of length of 30 mm and diameter of 2 mm. The pellets were fed into the barrel (L=300 mm, Diameter=12 mm), compressed and allowed to melt for 10 minutes before being extruded at a constant piston speed of 0.265 mm/s, which corresponds to a wall shear rate of 38.2 s⁻¹ at the given die diameter. The extrudate was passed through the wheels of the Rheotens located at 100 mm below the die exit and was pulled by the wheels downward at an acceleration rate of 2.4 mm/s². The force (in cN) exerted on the wheels was recorded as a function of the velocity of the wheels (mm/s). Melt strength was reported as the plateau force (cN) before the strand breaks or has significant draw resonance.

[0076] Dynamic-Mechanical Spectroscopy (DMS)

[0077] Melt rheology, frequency scans at constant temperature, was performed using a TA Instruments Advanced Rheometric Expansion System (ARES) rheometer equipped with 25 mm parallel plates under a nitrogen purge. Frequency sweeps were carried out at 190 °C for all samples 2.0 mm apart at a constant tension of 10%. The frequency range was 0.1 to 100 radians / second. The stress response in terms of amplitude and phase was analyzed, from which the storage modulus (G'), loss modulus (G''), and dynamic melt viscosity (η^*) were calculated.

[0078] Triple Detector Gel Permeation Chromatography (TDGPC)

[0079] Details of the TDGPC method can be found in U.S. Patent Application Number 17/632598, which is incorporated by reference herein.

[0080] GPC Deconvolution

[0081] The conventional GPC data was deconvoluted to give the most probable fit for two molecular weight components. There are a number of deconvolution algorithms available both

commercially and in the literature. These may lead to different answers depending upon the assumptions used. The algorithm summarized here is optimized for the deconvolution problem of the two most probable molecular weight distributions (plus an adjustable error term). In order to allow for the variations in the underlying distributions due to the macromer incorporation and small fluctuations in the reactor conditions (i.e. temperature, concentration) the basic functions were modified to incorporate a normal distribution term. This term allows the basis function for each component to be “smeared” to varying degrees along the molecular weight axis. The advantage is that in the limit (low LCB, perfect concentration and temperature control) the basis function will become a simple, most probable, Flory distribution.

[0082] Three components (j=1,2,3) are derived with the third component (j=3) being an adjustable error term. The GPC data must be normalized and properly transformed into weight fraction versus Log₁₀ molecular weight vectors. In other words, each potential curve for deconvolution should consist of a height vector, h_i, where the heights are reported at known intervals of Log₁₀ molecular weight, the h_i have been properly transformed from the elution volume domain to the Log₁₀ molecular weight domain, and the h_i are normalized. Additionally, these data should be made available for the Microsoft EXCEL™ application.

[0083] Several assumptions are made in the deconvolution. Each component, j, consists of a most probable, Flory, distribution which has been convoluted with a normal or Gaussian spreading function using a parameter, σ_j. The resulting, three basis functions are used in a Chi-square, X², minimization routine to locate the parameters that best fit the n points in h_i, the GPC data vector.

$$X^2(\mu_j, \sigma_j, w_j) = \sum_{i=1}^n \left[\sum_{j=1}^3 \left[\sum_{k=1}^{20} w_j \cdot M_i^2 \cdot \lambda_{j,k}^2 \cdot CumND_{j,k} \cdot e^{-\lambda_{j,k} \cdot M_i} \cdot \Delta \log_{10} M - h_i \right] \lambda_{j,k} \right]^2 =$$

$$\mu_j + \frac{k-10}{3} \cdot \sigma_j$$

10

[0084] The variable, CumND_{j,k}, is calculated using the EXCEL™ function “NORMDIST(x, mean, standard_dev, cumulative)” with the parameters set as follows:

$$x = \mu_j + (k-10) \cdot \sigma_j / 3$$

mean = μ_j

standard dev = σ_j

cumulative = TRUE

[0085] Table 1 below summarizes these variables and their definitions. The use of the EXCEL™ software application, Solver, is adequate for this task. Constraints are added to Solver to insure proper minimization.

[0086] Table 1: Variable Definitions

Variable Name	Definition
$\lambda_{j,k}$	Reciprocal of the number average molecular weight of most probable (Flory) distribution for component j, normal distribution slice k
σ_j	Sigma (square root of variance) for normal (Gaussian) spreading function for component j.
w_j	Weight fraction of component j
K	Normalization term ($1.0 / \log_e 10$)
M_i	Molecular weight at elution volume slice i
h_i	Height of $\log_{10}$ (molecular weight) plot at slice i
n	Number of slices in Log molecular weight plot
i	Log molecular weight slice index (1 to n)
j	Component index (1 to 3)
l. k	Normal distribution slice index
$\Delta \log_{10} M$	Average difference between $\log_{10} M_i$ and $\log_{10} M_{i-1}$ in height vs. $\log_{10} M$ plot

[0087] The 8 parameters that are derived from the Chi-square minimization are μ_1 , μ_2 , μ_3 , σ_1 , σ_2 , σ_3 , w_1 , and w_2 . The term w_3 is subsequently derived from w_1 and w_2 since the sum of the 3 components must equal 1. Table 2 is a summary of the Solver constraints used in the EXCEL program.

[0088] Table 2: Constraint summary

Description	Constraint
Maximum of fraction 1	$w_1 < 0.95$ (User adjustable)
Lower limit of spreading function	$\sigma_1, \sigma_2, \sigma_3 > 0.001$ (must be positive)
Upper limit of spreading function	$\sigma_1, \sigma_2, \sigma_3 < 0.2$ (User adjustable)
Normalized fractions	$w_1 + w_2 + w_3 = 1.0$

[0089] Additional constraints that are to be understood include the limitation that only $\mu_j > 0$ are allowed, although if Solver is properly initialized, this constraint need not be entered, as the Solver routine will not move any of the μ_j to values less than about 0.005. Also, the w_j are all understood to be positive. This constraint can be handled outside of Solver. If the w_j are understood to arise from the selection of two points along the interval $0.0 < P_1 < P_2 < 1.0$; whereby $w_1 = P_1$, $w_2 = P_2 - P_1$ and $w_3 = 1.0 - P_2$; then constraining P_1 and P_2 are equivalent to the constraints required above for the w_j .

[0090] Table 3 is a summary of the Solver settings under the Options tab.

[0091] Table 3: Solver settings

Label	Value or selection
Max Time (seconds)	1000
Iterations	100
Precision	0.000001
Tolerance (%)	5
Convergence	0.001
Estimates	Tangent
Derivatives	Forward
Search	Newton
ALL OTHER SELECTIONS	Not selected

[0092] A first guess for the values of μ_1 , μ_2 , w_1 , and w_2 can be obtained by assuming two ideal Flory components that give the observed weight average, number average, and z-average molecular weights for the observed GPC distribution.

$$\begin{aligned}
 M_{n, GPC} &= \left[w_1 \cdot \frac{1}{10^{\mu_1}} + w_2 \cdot \frac{1}{10^{\mu_2}} \right]^{-1} \\
 M_{w, GPC} &= \left[w_1 \cdot 2 \cdot 10^{\mu_1} + w_2 \cdot 2 \cdot 10^{\mu_2} \right] / M_{n, GPC} \\
 M_{z, GPC} &= \left[w_1 \cdot 6 \cdot 10^{\mu_1} + w_2 \cdot 6 \cdot 10^{\mu_2} \right] / M_{w, GPC} \\
 w_1 + w_2 &= 1
 \end{aligned}$$

[0093] The values of μ_1 , μ_2 , w_1 , and w_2 are then calculated. These should be adjusted carefully to allow for a small error term, w_3 , and to meet the constraints in Table II before entering into Solver for the minimization step. Starting values for σ_j are all set to 0.05.

[0094] Crystallization Elution Fractionation (CEF)

[0095] Comonomer distribution analysis, also commonly called short chain branching distribution (SCBD), is measured with Crystallization Elution Fractionation (CEF) (PolymerChar, Spain) (Monrabal et al, Macromol. Symp. 257, 71-79 (2007), which is incorporated herein by reference) equipped with an IR (IR-4 or IR-5) detector (PolymerChar, Spain) and 2-angle light scattering detector Model 2040 (Precision Detectors, currently Agilent Technologies). Distilled anhydrous ortho-dichlorobenzene (ODCB) with 600 ppm antioxidant butylated hydroxytoluene (BHT) was used as solvent. For the autosampler with the capability of N₂ purge, no BHT was added. A GPC guard column (20 microns, or 10 microns, 50X7.5 mm) (Agilent Technologies) is installed just before the IR detector in the detector oven. Sample preparation is done with an autosampler at 160 °C for 2 hours under shaking at 4 mg/ml (unless otherwise specified). The injection volume is 300 µl. The temperature profile of CEF is: crystallization at 3 °C/min from 110 °C to 30 °C, the thermal equilibrium at 30 °C for 5 minutes, elution at 3 °C/min from 30 °C to 140 °C. The flow rate during crystallization was at 0.052 ml/min. The flow rate during elution is at 0.50 ml/min. The data was collected at one data point/second.

[0096] The CEF column is packed by The Dow Chemical Company with glass beads at 125 µm + 6% (MO-SCI Specialty Products) with 1/8-inch stainless tubing. Glass beads are acid washed by MO-SCI Specialty by request from The Dow Chemical Company. Column volume is 2.06 ml. Column temperature calibration was performed by using a mixture of NIST Standard Reference Material Linear ethylene-based polymer 1475a (1.0 mg/ml) and Eicosane (2 mg/ml) in

ODCB. Temperature was calibrated by adjusting elution heating rate so that NIST linear ethylene-based polymer 1475a has a peak temperature at 101.0 °C, and Eicosane has a peak temperature of 30.0 °C. The CEF column resolution was calculated with a mixture of NIST linear ethylene-based polymer 1475a (1.0 mg/ml) and hexacontane (Fluka, purum $\geq 97.0\%$, 1mg/ml). A baseline separation of hexacontane and NIST ethylene-based polymer 1475a was achieved. The area of hexacontane (from 35.0 to 67.0 °C) to the area of NIST 1475a from 67.0 to 110.0 °C is 50 to 50, the amount of soluble fraction below 35.0 °C is less than 1.8 wt.%. The CEF column resolution is defined in Equation 9:

$$(a) \quad \text{Resolution} = \frac{\text{Peak Temperature}_{\text{NIST 1475A}} - \text{Peak Temperature}_{\text{Hexacontane}}}{\text{Width at Half Height}_{\text{NIST 1475A}} + \text{Width at Half Height}_{\text{Hexacontane}}} \geq 6.0$$

(Equation 9)

- (b) where the half height width is measured in temperature and resolution is at least 6.0.

[0097] The CEF instrument was equipped with an Agilent (Santa Clara, CA) Model 2040 2-angle light scattering detector, and the light scattering was calibrated using the 90 degree signal channel with a known homopolymer ethylene-based polymer standard of known molecular weight (approximately 120,000 g/mol). The IR (infrared) detector was also calibrated for mass response. Molecular weight (Mw(CEF)) at each elution point was calculated as a function of elution temperature in regions of adequate signal to noise. Area calculations (representing the total area of the 90 degree light scattering signal divided by the respective IR area and factored by the respective detector constants) was used to evaluate the weight-average molecular weight across regions of the elution temperature and to obtain a CEF-MW plot (Mw(CEF) vs. temperature curve). The area calculations have an inherent advantage of signal to noise over the continuous calculations. Both the IR and LS (light scattering) signals were subtracted from their baseline signal levels in accordance with normal chromatographic integration techniques.

[0098] A calculation of the “Critical Temperature (Tcritical),” the weight fraction of polymer and the weight-average molecular weight in the temperature range of up to and including the

critical temperature (Mw(CEF) of CEF fraction between 20 °C and Tcritical) were obtained as follows:

[0099] Obtain a CEF-SCBD (CEF-short chain branching distribution) plot using weight fraction (wtCEF(T)) at each temperature (T) from 20.0 °C to 119.9 °C with a temperature step increase of 0.2 °C, where

$$(c) \quad \int_{20.0}^{119.9} wt_{CEF}(T) dT = 1.00 \quad (\text{Equation 10})$$

[00100] Critical temperature is defined by the density of the resin (in g/cc) according to

$$T_{critical} (^{\circ}C) = 1108.1(^{\circ}C \cdot cc / g) \times density (g / cc) - 952.1(^{\circ}C) \quad (\text{Equation 11})$$

[00101] CEF weight fraction between 20 °C to Tcritical is calculated from CEF-SCBD as

$$(d) \quad \int_{20.0}^{T_{critical}} wt_{CEF}(T) dT \quad (\text{Equation 12})$$

[00102] Similarly, the weight-average molecular weight of the fraction from 20°C up to and including the critical temperature (Mw(CEF) of CEF fraction between 20 °C and Tcritical) was calculated as the area ratio of the sum of the 90 degree light scattering responses divided by the sum of the IR detector responses between 20 °C to Tcritical and factored for the calibrated detector constants. The molecular weight calculations and calibrations were performed in GPCOne® software.

[00103] Improved method for comonomer content analysis (iCCD)

[00104] Details of the ICCD method can be found in U.S. Patent Application Number 17/632598, which is incorporated by reference herein.

EXAMPLES

[00105] Embodiments will be further clarified by the following examples.

[00106] The preparation of several polymers according to the present methods was performed using benchtop experiments. Two samples Example 1 (EX-1) and Example 2 (EX-2) were

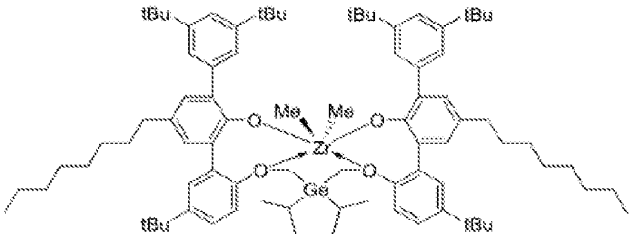
prepared by first feeding ethylene, octene, Isopar E (solvent), and Procatalyst 1 to a first reactor (also referred to as a precharger). The reaction constituents were introduced into the precharger under the conditions described in Table 4. The precharger effluent was then combined with additional feeds and further reacted, as described in more detail below.

Table 4 – Process Conditions for Examples

	Reactor 1 (Precharger)						
	Catalyst	Split	Tm	Isopar E Solvent Flow Rate	C2	C8	C2 exit
		[wt.%]	[°C]	[kg/h]	[kg/h]	[kg/h]	[g/l]
C2	Procatalyst 1	5.0	157	12.0	0.68	1.48	20.9
B2	Procatalyst 1	5.0	144	10.6	0.57	0.83	19.0

[00107] Referring to the process conditions in Table 4 above, the above polymers were produced in a multi-reactor system. The precharger reactor produced the high molecular weight component and included a catalyst system the procatalyst 1. The precharger reactor was a tubular reactor with stretched laminar flow profile. The residence time in the precharger was about 2 minutes.

[00108] Procatalyst A1



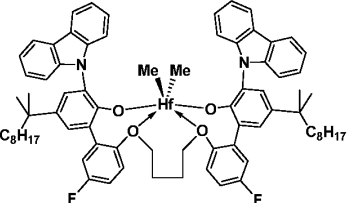
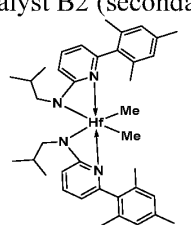
[00109] In addition to procatalyst A1, the catalyst system in the precharger included a MMAO-7 (CAS 206451-54-9) co-catalyst and deactivator. The catalyst was provided at a feed rate of about 50 g/h and includes a concentration of 0.08 mmol/kg.

[00110] The effluent from the precharger reactor 1 was then fed to reactor 2. Reactor 2 was operated at the conditions shown below in Table 5(a). The components of the catalyst system are shown below in Table 5(b). Precharger effluent C2 was used as the feed to prepare EX-1. Precharger effluent B2 was used as the feed to prepare EX-2.

Table 5(a)

Reactor Configuration	Type	Single Reactor
Comonomer type	Type	1-octene
Reactor Feed Solvent / Ethylene Mass Flow Ratio	g/g	4.6
Reactor Feed Comonomer / Ethylene Mass Flow Ratio	g/g	1.75
Reactor Feed Hydrogen / Ethylene Mass Flow Ratio	g/g	6.0E-05
Reactor Zn / Ethylene Mass Flow Ratio	g/g	4.2E-04
Reactor Temperature	°C	150
Reactor Pressure (verify correct units)	barg	34
Reactor Ethylene Conversion	%	89.1
Reactor % of Total Catalyst from Catalyst B2	Mole %	66.8
Co-catalyst 3 to Catalyst Molar Ratio (B to Catalyst Metal ratio)	Ratio	1.2
Co-catalyst 4 to Catalyst Molar Ratio (Al to Catalyst Metal ratio)	Ratio	7.6
Reactor Residence Time	min	12.8

Table 5(b): Catalysts and Co-Catalysts

Catalyst B1 (primary) 	Hafnium, [[2',2''-[1,4-butanediylbis(oxy-κO)]bis[3-(9H-carbazol-9-yl)-5-(1,1-dimethylnonyl)-5'-fluoro[1,1'-biphenyl]-2-olato-κO]](2-)]-dimethyl-
Catalyst B2 (secondary) 	Hafnium, dimethylbis[N-(2-methylpropyl)-6-(2,4,6-trimethylphenyl)-2-pyridinaminato-κN1, κN2]-
Co-catalyst 3	Bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) amine (RIBS-2) available from Boulder Scientific
Co-catalyst 4	Iso-butyl, methyl, branched, cyclic and linear modified methyl alumino-siloxane (MMAO), available from AkzoNobel
Chain Shuttling Agent	diethylzinc

[00111] The continuous solution polymerization reactor used for reaction 2 was a liquid full, non-adiabatic, isothermal, circulating, loop reactor, which mimics a continuously stirred tank reactor (CSTR) with heat removal. There was independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The total fresh feed stream to the reactor

(solvent, monomer, comonomer, and hydrogen) was temperature controlled to maintain a single solution phase, by passing the feed stream through a heat exchanger. The total fresh feed to the polymerization reactor was injected into the reactor at two locations, with approximately equal reactor volumes between each injection location. The fresh feed was controlled with each injector receiving half of the total fresh feed mass flow. The catalyst components are injected into the polymerization reactor. The primary catalyst component feed (catalyst 1 from Table 5(b)) was controlled to maintain the reactor monomer conversion at the specified target. The molar ratio of the secondary catalyst feed (catalyst 2 from Table 5(b) to total catalyst feed was adjusted to maintain the desired split between the polymer soft segment and hard segment. The co-catalyst 3 component was fed based on the calculated specified molar ratio to the catalyst components. The co-catalyst 4 component was fed to maintain a constant specified concentration in the reactor. Immediately following each reactor feed injection location, the feed streams were mixed. The contents of the reactor were continuously circulated through heat exchangers, with the temperature of the coolant side used for maintaining an isothermal reaction environment at the specified temperature. Circulation around the reactor loop was provided by a pump.

[00112] The reactor effluent entered a zone where it was deactivated with the addition of, and reaction with, a suitable reagent (water). At this same reactor exit location, other additives may be added for polymer stabilization. Following catalyst deactivation and additive addition, the reactor effluent entered a devolatilization system, where the polymer was removed from the non-polymer stream. The isolated polymer melt was pelletized and collected. The non-polymer stream passed through various pieces of equipment, which separate most of the ethylene that was removed from the system. Most of the solvent and unreacted comonomer was recycled back to the reactor after passing through a purification system. A small amount of solvent and comonomer was purged from the process. The properties of these produced polymers are shown in Table 6.

Table 6- Properties for Produced Polymers

REF	Fraction	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Dwn	Dzw	I ₂ (g/10 min)
EX-1	0.95	34643	94080	186429	2.72	1.98	
	0.05	429923	998679	1734295	2.32	1.74	
EX-1 Avg		36312	139310	741243	3,84	5,32	0.83

EX-2	0.95	35567	90783	166260	2.55	1.83	
	0.05	541905	1153115	1847718	2.13	1.60	
EX-2 Avg		37310	143900	839964	3.86	5.84	0.72

[00113] As can be seen in Table 6, the present examples EX-1 and EX-2 have a broad molecular weight distribution D_{wn} of greater than 3.6 and D_{zn} of greater than 4.5, which is known to have advantages in thermoplastic processing. It should be understood that EX-1_{Avg} and EX-2_{Avg} describe the entire polymer formed from the present methods, whereas the 0.95 and 0.05 fractions refer to the main block copolymer fraction and the high molecular weight copolymer fraction respectively. The properties of the individual fractions were determined according to the deconvolution methods described herein. Additional properties of EX-1 and EX-2 are given in Table 7. The density of the HMW fraction in EX-1 was determined to be 0.885 g/cc. The HMW fraction of EX-1 was determined to have 14.7 wt. % of octene comonomer. The density of the HMW fraction in EX-2 was determined to be 0.904 g/cc.

Table 7

REF	I ₂ (g/10 minutes)	I ₁₀ /I ₂	Density (g/cc)	Density HMW (g/cc)
EX-1	0.83	10.3	0.896	0.885
EX-2	0.72	11.1	0.886	0.904

CLAIMS

1. A method of producing ethylene-based polymer comprising first and second polymer fractions comprises:

reacting ethylene monomer and optionally C₃-C₁₂ α -olefin comonomer in solvent in the presence of a reaction A catalyst in at least one tubular reactor to produce the first polymer fraction reaching an exit temperature of this reaction zone below 160 °C, wherein the weight averaged molecular weight (Mw) of this first polymer fraction is larger than 500,000 g/mol;

introducing the first polymer fraction, ethylene monomer, optionally C₃-C₁₂ α -olefin comonomer, solvent, at least two reaction B catalysts, and a shuttling agent to at least one agitated solution polymerization reactor;

reacting the ethylene monomer and optionally C₃-C₁₂ α -olefin comonomer in solvent in the presence of the at least two reaction B catalysts and the shuttling agent in the at least one agitated solution polymerization reactor to produce a second polymer fraction; and

outputting effluent from the at least one agitated solution polymerization reactor, wherein the effluent comprises the ethylene-based polymer having the first and second polymer fractions, unreacted ethylene monomer, and optionally unreacted C₃-C₁₂ α -olefin comonomer,

wherein the ethylene-based polymer comprises 0.1 to 15 wt.% of the first polymer fraction and more than 70 wt.% of the second polymer fraction, and

wherein the ethylene-based polymer has a melt index (I₂) from 0.2 g/10 mins to 20 g/10 mins., a density between 0.880 g/cc to 0.908 g/cc and has an Mz/Mw greater than the Mw/Mn.

2. The method of claim 1, wherein the ethylene based polymer has a melt flow ratio I₂/I₁₀ of at least 9.

3. The method of any preceding claim, further comprising reacting the effluent of the at least one agitated solution polymerization reactor in the presence of a reaction C catalyst in a mixer downstream of the at least one agitated solution polymerization reactor wherein the reaction C catalyst facilitates further reaction of the unreacted ethylene monomer and optionally any

unreacted C₃-C₁₂ α -olefin comonomer to produce a third polymer fraction having a density and melt index (I₂) different from the second polymer fraction.

4. The method of claims 3, further comprising introducing a mixer effluent from the mixer to a tubular polymerization reactor, wherein the mixer effluent comprises the ethylene-based polymer having the first, second, and third polymer fractions.

5. The method of any preceding claim, wherein the at least one tubular reactor is a plug flow reactor and the at least one agitated solution polymerization reactor comprises at least one continuous stirred tank reactor (CSTR), at least one loop reactor, or combinations thereof.

6. The method of any preceding claim, wherein:

the ethylene monomer and C₃-C₁₂ α -olefin comonomer have a residence time R₁ in the at least one tubular reactor;

the ethylene monomer and optionally C₃-C₁₂ α -olefin comonomer have a residence time R₂ in the at least one agitated solution polymerization reactor; and

a ratio of R₁/R₂ is from 0.1 to 0.5.

7. The method of any preceding claim, wherein the at least one agitated solution polymerization reactor comprises an exit temperature of at least 150 °C.

8. The method of any preceding claim, wherein:

the reaction A catalyst in the at least one tubular reactor comprises a molecular catalyst;

the at least two reaction B catalysts in the at least one agitated solution polymerization reactor each comprise a molecular catalyst; and

the shuttling agent is diethyl zinc.

9. The method of any preceding claim, wherein the ethylene-based polymer comprises from 2 to 8 wt.% of the first polymer fraction and the ethylene-based polymer has a melt index (I₂) from 0.5 g/10 min to 5 g/10 min.

10. An elastic article comprising a polymer having a melt index (I_2) from 0.2 g/10 mins to 20 g/10 mins, a density between 0.880 g/cc to 0.908 g/cc and has an M_z/M_w greater than the M_w/M_n , wherein the polymer has been oriented to at least 4 times its original dimensions.
11. The elastic article of claim 10, wherein the polymer has been allowed to relax after having been oriented.