

**ETHYLENE COPOLYMER COMPOSITIONS AND
ARTICLES MADE THEREOF**

5 **CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of U.S. Provisional Application 63/518,006 filed August 07, 2023, the disclosure of which is hereby incorporated by reference in its entirety.

FIELD

10 [0002] Embodiments of the present invention generally relate to ethylene copolymers having distinct TREF peaks. Embodiments of the present invention further relate to blown films and TPO articles made from ethylene copolymers having distinct TREF peaks.

BACKGROUND

15 [0003] Ethylene-based copolymers are in high demand due to their high elasticity, flexibility, toughness, clarity, and processability. Such elastomers have a wide range of applications, including thermoplastic polyolefins (TPO), blown and cast films, injection molded containers and other goods, nonwoven fabrics, and hot-melt adhesives. Both high-viscosity and low-viscosity ethylene-based copolymers have been produced. Unfortunately, conventional ethylene-based copolymers fail to achieve a good balance of elasticity, stiffness, and flow characteristics. As a
20 result, customers of such ethylene-based copolymers often combine multiple ethylene-based elastomer products in pellet form at their production facilities to achieve the desired elasticity, stiffness, and flowability needed for certain end-use products such as auto TPOs, packaging films and other polymer modifications. The handling cost of combining so many products can be high due to the need for multiple conveyor systems.

25 [0004] Furthermore, mixing of different ethylene-based elastomer products can lead to pellet agglomeration and hence flow issues throughout the production facility. Polyolefins copolymers that are amorphous or low in crystallinity, such as plastomers, are also prone to agglomeration (clumping, chaining, bridging) during pellet drying-conveying-bagging steps in the manufacturing process or during transportation or during storage in warehouses. It is well known in the
30 manufacturing industry that producing a stable pellet of a low density resin (<0.870 g/cc) is a challenge due to adhesion/stickiness between pellets that are stored under normal environmental conditions. This situation can get worse if the low density resin is also a high flow material *i.e.*, > 5 MI.

[0005] There have been many attempts to improve shelf life and pellet stability in low density semi-crystalline or amorphous polymers. Resin producers typically treat the pellet surfaces with partitioning agents in combination with the dusting agents. Common methods have coated the pellets with anti-sticking agents such as CaSt₂, siloxanes or treated physical surface interaction through dusting with talc or polyethylene powder. For example, WO 2020/006396 A1, US 6852 787B1, US 5366645 (fumed SiO₂), US 10,544,295 B2 (HMA with cover film)) disclose a coating process that uses calcium stearate, polydimethyl siloxane, talc or polyethylene dusting. These methods, however, require additional equipment such as spray system, pellet water tank or dust delivery and handling systems.

[0006] Other attempts to mitigate agglomeration and improve pellet stability have tried multiple catalyst systems to create multimodal resins that are not as sticky. For example, US 10,023,669 B2 (LG Chem) discloses ethylene-octene compositions with three TREF peaks utilizing a mixture of two catalysts. US 10,961,335 B2 discloses ethylene-butene compositions with three CFC peaks utilizing a mixture of two metallocene catalysts. Other methods, such as disclosed in US 9,688,795 B2 and US 2019/0194503 A1, have tried improving pellet flowability in low density, low viscosity ethylene olefin copolymers and relate them to high comonomer content (wt% of material eluting below 65°C) from crystallization elution fractionation technique.

[0007] Other references of interest include: US20200010657; US11155658 B2; US10774205B2; US8569434 B2; and US 6,369,176 B1.

SUMMARY

[0008] In one embodiment, ethylene copolymers (“ECPs”) having at least two TREF peaks made from a single metallocene catalyst are provided herein. The ethylene copolymers can have at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units from one or more C₄ to C₂₀ alpha olefins, wherein the copolymer has a density in the range of 0.850 g/cc to 0.915 g/cc; MI in the range of 0.1 dg/min to 1000 dg/min; and MIR (I_{21.6} / I_{2.16}) in the range of 18 to 100. At least one TREF peak is a major fraction that accounts for at least 90 wt% of the copolymer and at least one other TREF peak is a minor fraction that accounts for less than 8 wt% of the copolymer and is found in the range of 60°C to 95°C.

[0009] Methods for making the ethylene copolymer having at least two TREF peaks made from a single metallocene catalyst by solution polymerization are also provided herein. In one embodiment, the method includes feeding ethylene, at least one comonomer, and a solvent in controlled proportions to a conduit upstream of a solution polymerization reactor; adding a single metallocene catalyst and an activator to the conduit; polymerizing at least a portion of the ethylene

and the at least one other monomer in the solution polymerization reactor to produce an ethylene pre-polymer having at least 5 wt% of the comonomer; feeding the ethylene pre-polymer to the solution polymerization reactor; feeding additional ethylene, comonomer, catalyst and activator in controlled proportions to the solution polymerization reactor and optionally additional solvent;
5 and operating the solution polymerization reactor to produce the ethylene copolymer, where at least one TREF peak is a major fraction that accounts for at least 90 wt% of the ethylene copolymer and wherein at least one other TREF peak is a minor fraction that accounts for less than 8 wt% of the ethylene copolymer and is found in the range of 60°C to 95°C.

[0010] In another embodiment, the method includes feeding ethylene, at least one comonomer,
10 and a solvent in controlled proportions to a solution polymerization reactor; adding a single metallocene catalyst and an activator to the solution polymerization reactor; polymerizing at least a portion of the ethylene and the at least one other monomer in the solution polymerization reactor to produce an ethylene copolymer having at least 5 wt% of the comonomer; flowing the ethylene pre-polymer from the solution polymerization reactor; and feeding additional ethylene in
15 controlled proportions to the ethylene copolymer within a conduit downstream of the solution polymerization reactor to provide the ethylene copolymer product where at least one TREF peak is a major fraction that accounts for at least 90 wt% of the ethylene copolymer product and wherein at least one other TREF peak is a minor fraction that accounts for less than 8 wt% of the ethylene copolymer product and is found in the range of 60°C to 95°C.

[0011] These and other features and attributes of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] 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, as briefly described below.

[0013] FIG. 1 shows TREF composition curves for an illustrative lower density copolymer made according to one or more embodiments described herein in comparison to commercially available copolymers having similar density and MI, namely, C3, C1 and C4.

[0014] FIG. 2 shows TREF composition curves for illustrative medium density copolymers made according to one or more embodiments described herein in comparison to commercially available
30 copolymers having similar density and MI, namely, a.) C5, C7 & S31 b.) C6, C8 & S22

[0015] FIG. 3 shows TREF composition curves for illustrative higher density copolymers made according to one or more embodiments described herein in comparison to commercially available copolymers having similar density and MI, namely, C9 and C10.

[0016] FIG. 4 shows the TREF elution temperature peaks (Peak 1 and Peak 2) as a function of ethylene wt% for various ethylene copolymers made according to one or more embodiments described herein.

5 [0017] FIG. 5 shows HD fraction (wt%) of the overall composition as a function of overall ethylene content (wt%), for various ethylene copolymers made according to one or more embodiments described herein.

[0018] FIG. 6 shows a schematic for an illustrative solution polymerization process suitable for making ethylene copolymers, in accordance with one or more embodiments described herein.

10 [0019] FIG. 7 shows the TREF high density fraction wt% versus the catalyst feeding rate relative to the activator, into the reactor, used to make the ethylene copolymers provided in the examples, in accordance with one or more embodiments described herein.

[0020] FIG. 8 depicts another schematic for an illustrative solution polymerization process suitable for making ethylene copolymers, in accordance with one or more embodiments described herein.

15 **DETAILED DESCRIPTION**

[0021] It is to be understood that the following disclosure describes several exemplary embodiments for implementing different features, structures, and/or functions of the invention. Exemplary embodiments of components, arrangements, and configurations are described below to simplify the present disclosure; however, these exemplary embodiments are provided merely
20 as examples and are not intended to limit the scope of the invention. Additionally, the present disclosure may repeat reference numerals and/or letters in the various exemplary embodiments and across the figures provided herein. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various exemplary embodiments and/or configurations discussed in the figures. Moreover, the exemplary embodiments presented below
25 can be combined in any combination of ways, *i.e.*, any element from one exemplary embodiment can be used in any other exemplary embodiment, without departing from the scope of the disclosure.

[0022] Ethylene copolymers, systems and methods for making same are provided. In one aspect, ethylene copolymers having two different density peaks ($\Delta > 0.020$ g/cc) produced using a single
30 catalyst using a single reactor are provided herein, and can be used in blown film, elastic and auto TPO applications. The ethylene copolymer typically has 0.1 wt% to 10 wt% of a higher density component, which does not significantly alter the composition's physical properties and end-use applications, but significantly increases its pellet stability and shelf life. Such (0.1 wt% - 10 wt%)

minor fraction that has a higher density can further have a high or low MI. In certain embodiments, the density of the minor fraction can range from about 0.865 g/cc to about 0.925 g/cc, and the density of the major fraction can range from about 0.850 g/cc to about 0.915 g/cc, so long as the density of the minor fraction is greater than the density of the major fraction by at least 0.020 g/cc, at least 0.025 g/cc, at least 0.030 g/cc, at least 0.035 g/cc, or at least 0.040 g/cc.

[0023] This minor HD fraction along with the major LD fraction significantly improves the elastomer's performance attributes for film, elastic and TPO applications, without significantly altering the overall product density, physical properties, and flow characteristics. This combination of high and low densities of any desired molecular weights of the minor component can be achieved in a single reactor loop through a catalyst/monomer injection port without the need for additional installation cost.

[0024] The method utilizes a single catalyst to prepare an ethylene copolymer with at least two TREF peaks in a single reactor. By "TREF" it is meant the Temperature Rising Elution Fractionation (TREF) technique as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., Vol. 20, pg. 441 (1982) and U.S. Pat. No. 5,008,204, which are incorporated by reference herein. In certain embodiments, the ethylene copolymer has at least two TREF peaks. At least one of those TREF peaks is a major fraction that accounts for at least 90 wt%, 92 wt% or 95 wt% of the copolymer and at least one other TREF peak is a minor fraction that accounts for less than 8 wt%, less than 6 wt%, less than 5 wt%, or less than 3 wt% of the copolymer and is found in the range of 60°C to 95°C. In certain embodiments, the major fraction TREF peak is found in the range of 0°C to 80°C. In certain other embodiments, the major fraction TREF peak can range can be 60-75°C, or 70-85°C, or 80-95°C.

[0025] The ethylene copolymer can be produced in a single reactor without the need for additional reactors and with a single catalyst without the need for additional catalysts. The resulting ethylene copolymer has excellent pellet stability with minimal or no anti-blocking agents added. For example, the resulting ethylene copolymer does not require any added pellet coating additives, such as metal stearates, siloxanes, talc dusting agents, but any of such additives could be used to improve pellet stability and/or tackiness. Similarly, the resulting ethylene copolymer does not require any added HDPE or LDPE.

[0026] The presence of a high density fraction does not affect the performance of the ethylene copolymer and does not require additional capital investment in the process. As such, the cost savings are significant. For one, capital cost is significantly reduced because only a single reactor and single catalyst is needed and two, the resulting additive costs are significant reduced.

[0027] It has also been surprisingly and unexpectedly discovered that the ethylene copolymer's molecular weight and density, if controlled appropriately, provides pellet stability by forming an encapsulated structure having a high density (HD) fraction with low molecular weight chains about its outer surface, providing a core-shell structure. Such pellets can provide films with reduced coefficients of friction because of the low molecular weight, higher density fraction that migrates to the surface of the film. The ethylene copolymers are particularly suitable for all molding, elastic and film applications.

[0028] Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges including the combination of any two values, e.g., the combination of any lower value with any upper value, the combination of any two lower values, and/or the combination of any two upper values are contemplated unless otherwise indicated. Certain lower limits, upper limits, and ranges appear in one or more claims below. All numerical values are "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0029] Additionally, certain terms are used throughout the following description and claims to refer to particular components. As one skilled in the art will appreciate, various entities can refer to the same component by different names, and as such, the naming convention for the elements described herein is not intended to limit the scope of the invention, unless otherwise specifically defined herein. Further, the naming convention used herein is not intended to distinguish between components that differ in name but not function.

[0030] In the following discussion and in the claims, the terms "including" and "comprising" are used in an open-ended fashion, and thus should be interpreted to mean "including, but not limited to." The phrase "consisting essentially of" means that the described/claimed composition does not include any other components that will materially alter its properties by any more than 5% of that property, and in any case does not include any other component to a level greater than 3 mass%.

[0031] The term "or" is intended to encompass both exclusive and inclusive cases, i.e., "A or B" is intended to be synonymous with "at least one of A and B," unless otherwise expressly specified herein.

[0032] The indefinite articles "a" and "an" refer to both singular forms (i.e., "one") and plural referents (i.e., one or more) unless the context clearly dictates otherwise. For example,

embodiments using “an olefin” include embodiments where one, two, or more olefins are used, unless specified to the contrary or the context clearly indicates that only one olefin is used.

[0033] The term “wt%” means percentage by weight, “vol%” means percentage by volume, “mol%” means percentage by mole, “ppm” means parts per million, and “ppm wt” and “wppm”
5 are used interchangeably and mean parts per million on a weight basis. All concentrations herein, unless otherwise stated, are expressed on the basis of the total amount of the composition in question.

[0034] The term “alpha-olefin” refers to any linear or branched compound of carbon and hydrogen having at least one double bond between the α and β carbon atoms. For purposes of this
10 specification and the claims appended thereto, when a polymer or copolymer is referred to as a “polyalphaolefin”, the alpha-olefin present in such polymer or copolymer is the polymerized form of the alpha-olefin. Also, the term “amorphous polyalphaolefin” refers to a polyalphaolefin in which the polymer chains are not arranged in ordered crystals.

[0035] The term “polymer” refers to any two or more of the same or different repeating
15 units/mer units or units. The term “homopolymer” refers to a polymer having units that are the same. The term “copolymer” refers to a polymer having two or more units that are different from each other, and can refer to interpolymers, terpolymers, etc. The term “terpolymer” refers to a polymer having three units that are different from each other. The term “different” as it refers to units indicates that the units differ from each other by at least one atom or are different
20 isomerically. Likewise, the definition of polymer, as used herein, includes homopolymers, copolymers, and the like. By way of example, when a copolymer is said to have a “propylene” content of 10 wt% to 30 wt%, it is understood that the repeating unit/mer unit or simply unit in the copolymer is derived from propylene in the polymerization reaction and the derived units are present at 10 wt% to 30 wt%, based on a weight of the copolymer.

25 [0036] The term “monomer” or “comonomer,” as used herein, refers to the monomer used to form the polymer, i.e., the unreacted chemical compound in the form prior to polymerization, and can also refer to the monomer after it has been incorporated into the polymer, also referred to herein as a “[monomer]-derived unit”.

[0037] The term “solution polymerization” refers to a polymerization process in which the
30 polymer is dissolved in a liquid polymerization medium, such as an inert solvent, monomer(s), or blends thereof. A solution polymerization is typically homogeneous. The term “homogeneous polymerization” refers to a polymerization process where the polymer product is dissolved in the polymerization medium. Such systems are preferably not turbid as described in J. Vladimir

Oliveira, C. Dariva, and J. C. Pinto, *Ind. Eng. Chem. Res.*, 29, 2000, 4627. A homogeneous polymerization process is typically a process where at least 90 wt% of the product is soluble in the reaction media.

[0038] As used herein, "Mn" refers to the number average molecular weight of the different polymers in a polymeric material, "Mw" refers to the weight average molecular weight of the different polymers in a polymeric material, and "Mz" refers to the z average molecular weight of the different polymers in a polymeric material. The terms "molecular weight distribution" (MWD) and "polydispersity index" (PDI) are used interchangeably to refer to the ratio of Mw to Mn. Unless otherwise noted, all molecular weights (e.g., Mw, Mn, Mz) are reported in units of g/mol. Also, the term "broad orthogonal comonomer distribution" (BOCD) refers to a positively sloped comonomer content profile along the log Mw of a polymer.

[0039] In the following discussion, reference to a carbon-containing compound such as a hydrocarbon may be made in the shorthand form of "C n ", where n refers to the number of carbon atoms in the compound regardless of the number of hydrogen or heteroatoms in the compound. If a plus or minus sign is used, it designates a range of carbon atoms containing n carbon atoms or more or n carbon atoms or less. For example, "C 9^{+} " refers to compounds such as hydrocarbons having 9 or more carbon atoms, and "C 9^{-} " refers to compounds such as hydrocarbons having 9 or fewer carbon atoms.

[0040] Nomenclature of elements and groups thereof used herein are pursuant to the Periodic Table used by the International Union of Pure and Applied Chemistry after 1988. An example of the Periodic Table is shown in the inner page of the front cover of *Advanced Inorganic Chemistry*, 6th Edition, by F. Albert Cotton et al. (John Wiley & Sons, Inc., 1999).

[0041] A more detailed description of the ethylene copolymers, methods for making, and films made therefrom will now be provided. Each of the appended claims defines a separate invention, which for infringement purposes is recognized as including equivalents to the various elements or limitations specified in the claims. Depending on the context, all references to the "invention" may in some cases refer to certain specific embodiments only. In other cases, it will be recognized that references to the "invention" will refer to subject matter recited in one or more, but not necessarily all, of the claims. Each of the inventions will now be described in greater detail below, including specific embodiments, versions and examples, but the inventions are not limited to these embodiments, versions or examples, which are included to enable a person having ordinary skill in the art to make and use the inventions, when the information in this disclosure is combined with publicly available information and technology.

[0042] The ethylene copolymers provided herein contain ethylene and at least one other C4-C20 comonomer. The ethylene content of the lower ethylene content fraction can range from a low of 54 wt% to a high of 85 wt%. The ethylene content of the higher ethylene content fraction can range from a low of 60 wt% to a high of 95 wt%. The ethylene content of the overall copolymer can range from a low of 54 wt% to a high of 85 wt%.

Comonomer

[0043] The at least one other comonomer can include any one or more C4 to C20 olefins. The C4 to C20 comonomers can be linear, branched, or cyclic. Suitable C4 to C20 cyclic olefins can be strained or unstrained, monocyclic or polycyclic, and can optionally include heteroatoms and/or one or more functional groups. The reactor C2 concentration can range from 0.1 to 40.0 wt% while the reactor comonomer concentration can range from 0.1 to 40.0 wt%, based on the total contents of the reactor.

[0044] Specific examples of comonomers include butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5 -cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, preferably norbornene, norbornadiene, and dicyclopentadiene. Preferred comonomers are butene and octene.

[0045] One or more dienes (diolefin comonomer) can be added to the polymerization process. The diene can be present in the polymer produced herein at up to 10 wt%, preferably at 0.00001 to 8.0 wt%, preferably 0.002 to 8.0 wt%, even more preferably 0.003 to 8.0 wt%, based upon the total weight of the composition. In some embodiments, 500 ppm or less of diene is added to the polymerization, preferably 400 ppm or less, preferably 300 ppm or less. In other embodiments, at least 50 ppm of diene is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

[0046] Suitable diolefin comonomers include any hydrocarbon structure, preferably C4 to C30, having at least two unsaturated bonds, where at least one of the unsaturated bonds are readily incorporated into a polymer chain during chain growth. It is further preferred that the diolefin comonomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). More preferably, the diolefin comonomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Specific examples of preferred dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene,

tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (M_w less than 1000 g/mol). Preferred cyclic dienes include cyclopentadiene, 5-vinyl-2-norbornene, norbornadiene, 5-ethylidene-2-norbornene, divinylbenzene, and dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

10 **[0047]** The ethylene copolymers can have a melt index (MI) of 0.1 dg/min to about 1,000 dg/min, as measured according to ASTM D1238 (190°C/2.16 kg). The melt index can also range from a low of about 0.1, 0.5, or 1.0 to a high of about 500, 700, or 1,000 dg/min. The melt index can also range from a low of about 5, 10 or 20 to a high of about 120, 335, or 450 dg/min.

[0048] The ethylene copolymers can also have a broad melt index ratio (MIR) or ($I_{21.6}/I_{2.16}$) 15 ranging from 18.0 to about 100.0, as measured according to ASTM D1238 (190°C/2.16 kg). The MIR can also range from a low of about 20, 30, or 40 to a high of about 60, 80, or 95.

[0049] The ethylene copolymers can have a density of from 0.850 g/cc to 0.915 g/cc, as measured according to ASTM D1505, which indicates that they can serve as plastomers having the combined qualities of elastomers and plastics. The ethylene copolymers can also have a 20 density of about 0.860 g/cc to 0.880 g/cc. The density can range from a low of about 0.850, 0.855, 0.860, 0.865, or 0.870 to a high of about 0.874, 0.876, 0.880, 0.900, or 0.915 g/cc.

[0050] The ethylene copolymers can have long chain branching that is defined by g'_{avg} of between 0.7 and 0.99, as measured by GPC-4D. The ethylene copolymer can also have a g'_{Mz+1} to g'_{avg} ratio of 0.9 to 1.0. This ratio can also range from a low of 0.91, 0.92 or 0.93 to a high 25 of 0.97, 0.98, or 0.99.

[0051] The ethylene copolymers can have a reactivity ratio ($r_A = k_{AA}/k_{AB}$) of 0.9 or less. The reactivity ratio can also range from 0.2 to 0.8. The reactivity ratio can also range from a low of 0.2, 0.3, or 0.35 to a high of 0.5, 0.65, or 0.8. The reactivity ratio can also be 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 or 0.8.

30 **[0052]** The ethylene copolymers can have a MWD of 1.2 to 5.0. The MWD can also range from 1.5 to 4.8; 1.8 to 4.7; 2.0 to 4.5 and 2.2 to 4.4.

[0053] The ethylene copolymers can have a long branching index (g'_{avg}) as measured from GPC-4D from 0.850 to 0.990; 0.860 to 0.980; 0.870 to 0.970; 0.870 to 0.960; or 0.88 to 0.950.

Catalyst System

[0054] The catalyst system for polymerizing the ethylene copolymers can include a single bridged metallocene compound having a single substituted carbon or silicon atom bridging two ancillary monanionic ligands, such as substituted or unsubstituted cyclopentadienyl-containing (Cp) ligands and/or substituted and unsubstituted Group 13-16 heteroatom ligands, of the metallocene metal centers. The bridge substituents can be substituted aryl groups, the substituents including at least one solubilizing hydrocarbylsilyl substituent located on at least one of the aryl group bridge substituents. Substituents present on the cyclopentadienyl and/or heteroatom ligands can include C₁-C₃₀ hydrocarbyl, hydrocarbylsilyl, or hydrofluorocarbyl groups as replacements for one or more of the hydrogen groups on those ligands, or those on fused aromatic rings on the cyclopentadienyl rings. Aromatic rings can be substituents on the cyclopentadienyl ligands and are inclusive of the indenyl and fluorenyl derivatives of cyclopentadienyl groups and their hydrogenated counterparts. Such aromatic rings typically include one or more aromatic ring substituents selected from linear, branched, cyclic, aliphatic, aromatic or combined structure groups, including fused-ring or pendant configurations. Examples include methyl, isopropyl, n-propyl, n-butyl, isobutyl, tertiary butyl, neopentyl, phenyl, n-hexyl, cyclohexyl, benzyl, and adamantyl. As used herein, the term "hydrocarbon" or "hydrocarbyl" is meant to include those compounds or groups that have essentially hydrocarbon characteristics but optionally contain not more than about 10 mol% non-carbon heteroatoms, such as boron, silicon, oxygen, nitrogen, sulfur, and phosphorous. Additionally, the term is meant to include hydrofluorocarbyl substituted groups. "Hydrocarbylsilyl" is exemplified by, but not limited to, dihydrocarbyl- and trihydrocarbylsilyls, where the preferred hydrocarbyl groups are C₁-C₃₀ substituent hydrocarbyl, hydrocarbylsilyl or hydrofluorocarbyl substituents for the bridging group phenyls. For heteroatom containing catalysts, see International Publication No. WO 92/00333. Also, the use of hetero-atom containing rings or fused rings, where a non-carbon Group 13, 14, 15 or 16 atom replaces one of the ring carbons is considered herein to be within the terms "cyclopentadienyl", "indenyl", and "fluorenyl". See, for example, the background and teachings of International Publication Nos. WO 98/37106 and WO 98/41530, which are incorporated herein by reference.

[0055] Particularly suitable cyclopentadienyl-based complexes are the compounds, isomers, or mixtures, of (para-trimethylsilylphenyl)(para-n-butylphenyl)methylene (fluorenyl) (cyclopentadienyl) hafnium dimethyl, di(para-trimethylsilylphenyl)methylene (2,7-di-tertbutyl fluorenyl) (cyclopentadienyl) hafnium dimethyl, di(para-triethylsilylphenyl)methylene (2,7-di-tertbutyl-fluorenyl) (cyclopentadienyl) hafnium dimethyl, (para-triethylsilylphenyl) (para-t-

butylphenyl) methylene (2,7-di tertbutyl fluorenyl) (cyclopentadienyl) hafnium dimethyl or dibenzyl, and di(para-triethylsilyl-phenyl)methylene (2,7-dimethylfluorenyl)(cyclopentadienyl) hafnium dimethyl or dibenzyl.

Activators

5 **[0056]** The bridged metallocene compounds can be activated for polymerization catalysis in any manner sufficient to allow coordination or cationic polymerization. This can be achieved for coordination polymerization when one ligand can be abstracted and another will either allow insertion of the unsaturated monomers or will be similarly abstractable for replacement with a ligand that allows insertion of the unsaturated monomer (labile ligands), e.g., alkyl, silyl, or
 10 hydride. The traditional activators of coordination polymerization art are suitable, for example, Lewis acids such as alumoxane compounds, and ionizing, anion precursor compounds that abstract one so as to ionize the bridged metallocene metal center into a cation and provide a counter-balancing noncoordinating anion.

[0057] In any embodiment, the activators of the catalyst system disclosed herein can include an
 15 anionic component, [Y]. In any embodiment, the anionic component can be a non-coordinating anion (NCA), having the formula $[B(R^4)_4]^-$, where R^4 is an aryl group or a substituted aryl group, of which the one or more substituents are identical or different and are selected from the group consisting of alkyl, aryl, a halogen atom, halogenated aryl, and haloalkylaryl groups. The substituents can be perhalogenated aryl groups, or perfluorinated aryl groups, including,
 20 perfluorophenyl, perfluoronaphthyl and perfluorobiphenyl.

[0058] Together, the cationic and anionic components of the catalysts systems disclosed herein form an activator compound. In any embodiment, the activator can be N,N-dimethylanilinium-tetra(perfluorophenyl)borate, N,N-dimethylanilinium-tetra(perfluoronaphthyl)borate, N,N-dimethylanilinium-tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium-tetrakis(3,5-
 25 bis(trifluoromethyl)phenyl)borate, triphenylcarbenium-tetra(perfluorophenyl)borate, triphenylcarbenium-tetra(perfluoronaphthyl)borate, triphenylcarbenium-tetrakis(perfluorobiphenyl)borate, or triphenylcarbenium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

[0059] See also International Publication Nos. WO/2000/024793, WO/2021/162748, and
 30 WO/2013/134038, each of which is incorporated herein by reference, for detailed descriptions of suitable catalyst systems and activators.

Methods for Making

[0060] The ethylene copolymers can be made using a solution polymerization process. Preferably, the solution polymerization process is a bulk polymerization process, which refers to a polymerization process in which the monomers and/or comonomers being polymerized are used
5 as a solvent or diluent using little or no inert solvent as a liquid or diluent. A small fraction of inert solvent might be used as a carrier for a catalyst and a scavenger. A suitable solution polymerization process is generally described in more detail in U.S. Patent Nos. 9,359,535, 7,470,118, 7,226,553; and 7,033,152, which are incorporated by reference herein in their entirety.

[0061] Any suitable reaction system for solution polymerization can be used. WO
10 2017/058385A1, for example, describes a solution polymerization process using single or multiple spiral heat exchanger systems for continuous polymerization of C2 to C40 olefins, which can also be used and is also incorporated by reference herein in its entirety.

[0062] In one embodiment, the reactor system can include one or more plug flow reactors, and each plug flow reactor can be or can include at least one spiral heat exchanger. The spiral heat
15 exchanger can include a body formed by at least one spiral sheet wound to form spirals which are arranged radially around an axis of the spiral heat exchanger. The spirals can form at least one flow channel for flow of a heat exchange medium, and the spirals can be enclosed by a substantially cylindrical shell. Also, the cylindrical shell can include at least one inlet and at least one outlet in fluid communication with the at least one flow channel for providing and removing
20 the heat exchange medium.

[0063] The monomer, comonomer, catalyst system, and copolymer product flow in an axial direction through channels formed in between the spirals of the heat exchanger. The monomer, comonomer, catalyst system, and copolymer product flow in a cross-flow direction relative to the spirals of the at least one spiral heat exchanger. As used herein, "cross-flow" direction refers to a
25 flow substantially orthogonal in direction to the spirals of the at least one spiral heat exchanger. Substantially orthogonal can include flow of the monomer, comonomer, catalyst system, and copolymer product at an angle of 70° to 110°, preferably 80° to 100°, more preferably 85° to 95°, even more preferably 88° to 92°, or most preferably 90°, with respect to the spirals of the at least one spiral heat exchanger.

[0064] The at least one spiral exchanger can be oriented in a substantially vertical direction such that the monomer, comonomer, catalyst system, and copolymer product flow in a substantially vertical direction through the at least one spiral heat exchanger. The orientation of the at least one spiral heat exchanger is not limited to such a vertical orientation but rather can be oriented in any
30

direction so long as the feed and product flow through the at least one spiral heat exchanger in a cross-flow direction relative to the spirals of the at least one spiral heat exchanger. For example, the at least one spiral heat exchanger can be oriented in a substantially horizontal direction such that the monomer, comonomer, catalyst system, and copolymer product flow through the at least one spiral heat exchanger in a substantially horizontal direction.

[0065] Alternatively, the at least one spiral heat exchanger can include multiple spiral heat exchangers, e.g., at least 2, at least 3, at least 4, at least 5, at least 6, at least 7, at least 8, at least 9, at least 10, at least 11, at least 12, at least 13, at least 14, at least 15, at least 16, at least 17, at least 18, at least 19, at least 20, at least 21, at least 22, at least 23, at least 24, etc.

[0066] The at least one spiral heat exchanger used in the processes described herein can be any suitable spiral heat exchanger known in the art. Non-limiting examples of suitable spiral heat exchangers include those described in US Patent Nos. 8,622,030; 8,075,845; 8,573,290; 7,640,972; 6,874,571; 6,644,391; 6,585,034; and 4,679,621; US Publication Nos. 2010/0170665; 2010/0008833; 2002/0092646; and 2004/0244968, and International Publication No. WO/2017/058385, each of which are incorporated herein by reference. Additionally or alternatively, the at least one spiral heat exchanger can have a surface area to volume ratio of about 20-30 ft²/ft³. Advantageously, the spiral heat exchanger can have an open channel height of 0.5 to 30 feet, preferably 1 to 25 feet, 3 to 20 feet, 5 to 15 feet, or 5 to 10 feet.

[0067] The heat exchange medium that flows through the spirals of the heat exchanger can be any suitable heat exchange medium known in the art. Particularly useful heat exchange media are those stable at the reaction temperatures and typically include those stable at 200°C or more. Examples of heat transfer media include water and other aqueous solutions, oil (e.g., hydrocarbons, such as mineral oil, kerosene, hexane, pentane, and the like), and synthetic media, such as those commercially available from The Dow Chemical Company (Midland, Michigan) under the trade name DOWTHERM™, such as grades A, G, J, MX, Q, RP, and T. If water is used, then the water is preferably under a suitable amount of pressure to prevent boiling. Preferably, the heat exchange medium flows through the spirals at a temperature lower than a temperature of the feed stream. Additionally, or alternatively, the heat exchange medium can flow through the spirals at a temperature above a precipitation point of the polymer. For example, the heat exchange medium can flow through the spirals at a temperature of 100°C to 150°C, preferably 120°C to 140°C, or more preferably 130°C.

[0068] In various aspects, the monomer, the comonomer, the catalyst system, and the polymer can be maintained substantially as a single liquid phase under polymerization conditions.

Preferably, the flow of the liquid through the at least one spiral heat exchanger can be substantially laminar or near-laminar. Preferably, the Reynolds number of the flow of the liquid can be > about 0.1, > about 1.0, > about 10.0, > about 20.0, > about 30.0, > about 40.0, > about 50.0, > about 60.0, > about 70.0, > about 80.0, > about 90.0, > about 100, > about 200, > about 300, > about 400, > about 500, > about 600, > about 700, > about 800, > about 900, > about 1,000, > about 1,100, > about 1,200, > about 1,300, > about 1,400, > about 1,500, > about 1,600, > about 1,700, > about 1,800, > about 1,900, > about 2,000, > about 2,100, or about 2,200. Additionally or alternatively, the Reynolds number of the flow of the liquid can be < about 40.0, < about 50.0, ≤ about 60.0, ≤ about 70.0, ≤ about 80.0, ≤ about 90.0, ≤ about 100, ≤ about 200, < about 300, ≤ about 400, ≤ about 500, ≤ about 600, ≤ about 700, ≤ about 800, ≤ about 900, ≤ about 1,000, ≤ about 1,100, ≤ about 1,200, ≤ about 1,300, ≤ about 1,400, ≤ about 1,500, ≤ about 1,600, ≤ about 1,700, ≤ about 1,800, ≤ about 1,900, ≤ about 2,000, ≤ about 2,100 or < about 2,200. Ranges expressly disclosed include combinations of any of the above-enumerated values, e.g., about 0.1 to about 2,200, about 1.0 to about 1,400, about 1.0 to about 100, about 50.0 to about 900, etc.

Preferably, the Reynolds number of the liquid is about 0.1 to about 2,200, preferably about 1.0 to about 1,000, preferably about 1.0 to about 100, more preferably about 1.0 to about 50. Reynolds number is calculated using the hydraulic diameter (Dh) and the hydraulic diameter (Dh) and is defined as $Dh=4A/P$, where A is the cross-sectional area and P is the wetted perimeter of the cross-section of a channel in the spiral heat exchanger. Zero shear viscosity is used for Reynolds number calculation when a non-Newtonian fluid is used.

[0069] The polymerization process can be conducted at a temperature of from about 50°C to about 220°C, preferably from about 70°C to about 210°C, preferably from about 90°C to about 200°C, preferably from about 100°C to about 190°C, or preferably from about 130°C to about 160°C. The polymerization process can be conducted at a pressure of from about 120 to about 1,800 psi (827 to 12,411 kPa), preferably from about 200 to about 1,000 psi (1,379 to 6,895 kPa), preferably from about 300 to about 800 psi (2,068 to 5,516 kPa).

[0070] In various aspects, residence time in the spiral heat exchanger can be up to 24 hours or longer, typically from about 1 minute to about 15 hours. The residence time is preferably from about 2 minutes to about 1 hour, from about 3 to about 30 minutes, from about 5 to about 25 minutes, or from about 5 to about 20 minutes.

[0071] In some embodiments, hydrogen can be present during the polymerization process at a partial pressure of from about 0.001 to about 50.000 psig (0.007 to 346 kPa), preferably from about 0.010 to about 25.000 psig (0.069 to 172 kPa), more preferably from about 0.100 to about

10.000 psig (0.689 to 483 kPa). Alternatively, the hydrogen concentration in the feed can be 500 wppm or less, preferably 200 wppm or less.

[0072] In various aspects, the cement concentration of the polymer produced can range from about 2 wt% to about 40 wt%, preferably from about 6 wt% to about 40 wt%, or more preferably
5 from about 6 wt% to about 25 wt%. The cement concentration can also be at least 5%, 8%, 10%, 15%, or 25% and less than 40 wt%. "Cement concentration" is herein defined to be the weight of the polymer produced based on the weight of the total solvent (e.g., monomer, comonomer, and/or solvent).

[0073] The monomer, comonomer, catalyst system, and solvent can be added and reacted within
10 the reactor to produce the ethylene copolymer product. In other embodiments, as explained below in the experimental section and with reference to FIGs. 6 and 8, a portion of the monomer, comonomer, and/or catalyst system can be pre-mixed and reacted either upstream of the reactor or downstream of the reactor in order to influence the ethylene to comonomer weight ratios thereby creating the high density (HD) fractions in the copolymer product. For example, a minor
15 portion of the monomer, comonomer, catalyst system can be reacted in a conduit section upstream of the reactor to produce a pre-polymer, as depicted in FIG. 6, that is then fed to the reactor system. In certain embodiments, anywhere from 5-45 wt % of the total amount of catalyst and activator can be added to the conduit upstream of the solution polymerization reactor. From 5-45 wt % of the total amount of ethylene can be added to the conduit upstream of the solution polymerization
20 reactor. From 5-45 wt % of the total amount of comonomer can added to the conduit upstream of the solution polymerization reactor. At least 90 wt % of the ethylene copolymer can be made in the solution polymerization reactor and the balance of the ethylene copolymer can be made in the conduit upstream of the solution polymerization reactor. Alternatively, the monomer alone or in combination with additional comonomer and/or catalyst and/or activator can be added
25 downstream of the reactor to influence the ethylene to comonomer weight ratios, thereby creating the high density (HD) fractions in the copolymer product, as depicted in FIG. 8. In certain embodiments, anywhere from 5-45 wt % of the total amount of catalyst and activator can be added to the conduit downstream of the solution polymerization reactor. From 5-45 wt % of the total amount of ethylene can be added to the conduit downstream of the solution polymerization reactor.
30 From 5-45 wt % of the total amount of comonomer can added to the conduit downstream of the solution polymerization reactor. From at least 90 wt % of the ethylene copolymer can be made in the solution polymerization reactor and the balance of the ethylene copolymer can be made in the conduit downstream of the solution polymerization reactor.

[0074] The polymerization process can further include recycling at least a portion of the solvent, the monomer/comonomer, the catalyst system, and the polymer exiting the reactor back through the reactor. Polymer can be produced with a recycle ratio ranging from about 3 to about 50, preferably from about 3 to about 30, or more preferably from about 3 to about 20. The recycle ratio is herein defined to be the ratio between the flow rate of the recycle loop just prior to entry into the spiral heat exchanger (alone or in series) divided by the flow rate of fresh feed to the spiral heat exchanger (alone or in series).

[0075] The ethylene copolymers can have a unique combination of any two or more of the following attributes:

- Density of 0.850 g/cc to 0.915 g/cc;
- MI of 0.1 dg/min to 1000 dg/min;
- MIR ($I_{21.6} / I_{2.16}$) of 18 to 100;
- TREF elution peak 1 is a major fraction accounting for more than 90 wt% of the overall composition;
- TREF elution peak 1 of 0°C to 80°C;
- TREF elution peak 2 is a minor fraction with less than 8 wt% of the overall composition;
- TREF elution peak 2 of 60°C to 95°C;
- MWD of 1.2 to 5.0; and
- long branching index (g' avg) as measured from GPC-4D from 0.850 to 0.990.

Other Test Methods

[0076] Film thickness, reported in microns, is measured using a Measuretech Series 200 instrument. The instrument measures film thickness using a capacitance gauge. For each film sample, ten film thickness data points are measured per inch of film as the film is passed through the gauge in a transverse direction. From these measurements, an average gauge measurement is determined and reported.

[0077] Gel Permeation Chromatography (GPC) is a liquid chromatography technique used to measure the molecular weight and polydispersity of polymers.

[0078] Unless otherwise indicated, the distribution and the moments of molecular weight (e.g., Mw, Mn, Mz, Mw/Mn) and the comonomer content (e.g., C2, C3, C6) is determined by using a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a multiple-channel band-filter based Infrared detector IR5, an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10- μ m Mixed-B LS columns are used to provide polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB mixture is filtered through a 0.1- μ m Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 mL/min, and the nominal injection volume is 200 μ L. The whole system including transfer lines, columns, and detectors is contained in an oven maintained at 145°C. The polymer sample is weighed and sealed in a standard vial with 80- μ L flow marker (heptane) added to it. After loading the vial in the autosampler, polymer is dissolved in the instrument with 8 mL added TCB solvent. The polymer is dissolved at 160°C with continuous shaking for about 1 hour for polyethylene samples or about 2 hours for polypropylene samples. The TCB densities used in concentration calculation is 1.463 g/ml at room temperature and 1.284 g/mL at 145°C. The sample solution concentration is from 0.2 to 2.0 mg/mL, with lower concentrations being used for higher molecular weight samples. The concentration (c), at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal intensity (I), using the following equation: $c = \beta I$, where β is the mass constant. The mass recovery can be calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass, which is equal to the pre-determined concentration multiplied by injection loop volume. The conventional molecular weight (IR molecular weight) is determined by combining universal calibration relationship with the column calibration, which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10,000,000 gm/mole. The molecular weight at each elution volume is calculated with (1):

$$\log M = \frac{\log(K_{PS}/K)}{\alpha + 1} + \frac{\alpha_{PS} + 1}{\alpha + 1} \log M_{PS} \quad \text{EQ. 1}$$

[0079] Where the variables with subscript "PS" stand for polystyrene while those without a subscript are for the test samples. In this method, $\alpha_{PS} = 0.67$ and $K_{PS} = 0.000175$ while α and K for other materials are as calculated and published in literature (Sun, T. et al. Macromolecules 2001, 34, 6812), except that for purposes of this invention and claims thereto, $\alpha = 0.705$ and $K = 0.0002288$ for linear propylene polymers, $\alpha = 0.695$ and $K = 0.000181$ for linear butene polymers,

α is 0.695 and K is $0.000579 \cdot (1 - 0.0087 \cdot w_{2b} + 0.000018 \cdot (w_{2b})^2)$ for ethylene-butene copolymer where w_{2b} is a bulk weight percent of butene comonomer, α is 0.695 and K is $0.000579 \cdot (1 - 0.0075 \cdot w_{2b})$ for ethylene-hexene copolymer where w_{2b} is a bulk weight percent of hexene comonomer, and α is 0.695 and K is $0.000579 \cdot (1 - 0.0077 \cdot w_{2b})$ for ethylene-octene copolymer where w_{2b} is a bulk weight percent of octene comonomer, and $\alpha = 0.695$ and $K = 0.000579$ for all other linear ethylene polymers. Concentrations are expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity (hence K in the Mark-Houwink equation) is expressed in dL/g, unless otherwise noted.

[0080] The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH₂ and CH₃ channel calibrated with a series of polyethylene and propylene homo/copolymer standards whose nominal value are predetermined by NMR or FTIR. In particular, this provides the methyls per 1000 total carbons (CH₃/1000TC) as a function of molecular weight. The short-chain branch (SCB) content per 1000TC (SCB/1000TC) can be then computed as a function of molecular weight by applying a chain-end correction to the CH₃/1000TC function, assuming each chain to be linear and terminated by a methyl group at each end. The weight % comonomer can be then obtained from the following expression in which f is 0.3, 0.4, 0.6, 0.8, and so on for C3, C4, C6, C8, and so on co-monomers, respectively:

$$w_2 = f \cdot \text{SCB}/1000\text{TC} \quad \text{EQ. 2}$$

[0081] The bulk composition of the polymer from the GPC-IR and GPC-4D analyses is obtained by considering the entire signals of the CH₃ and CH₂ channels between the integration limits of the concentration chromatogram. First, the following ratio is obtained.

$$\text{Bulk IR ratio} = \frac{\text{Area of CH}_3 \text{ signal within integration limits}}{\text{Area of CH}_2 \text{ signal within integration limits}} \quad \text{EQ. 3}$$

[0082] Then the same calibration of the CH₃ and CH₂ signal ratio, as mentioned previously in obtaining the CH₃/1000TC as a function of molecular weight, is applied to obtain the bulk CH₃/1000TC. A bulk methyl chain ends per 1000TC (bulk CH₃end/1000TC) is obtained by weight-averaging the chain-end correction over the molecular-weight range. Then,

$$w_{2b} = f \cdot \text{bulk CH}_3/1000\text{TC} \quad \text{EQ. 4}$$

$$\text{bulk SCB}/1000\text{TC} = \text{bulk CH}_3/1000\text{TC} - \text{bulk CH}_3\text{end}/1000\text{TC} \quad \text{EQ. 5}$$

[0083] And bulk SCB/1000TC are converted to bulk w2 in the same manner as described above.

[0084] The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (M) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (Light Scattering from Polymer Solutions; Huglin, M. B., Ed.; Academic Press, 1972):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c \quad \text{EQ. 6}$$

[0085] Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration determined from the IR5 analysis, A_2 is the second virial coefficient, $P(\theta)$ is the form factor for a monodisperse random coil, and KO is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \quad K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \quad \text{EQ. 7}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system, $n = 1.500$ for TCB at 145°C , and $\lambda = 665 \text{ nm}$. For analyzing ethylene homopolymers, ethylene-hexene copolymers, and ethylene-octene copolymers, $dn/dc = 0.1048 \text{ ml/mg}$ and $A_2 = 0.0015$; for analyzing ethylene-butene copolymers, $dn/dc = 0.1048 * (1 - 0.00126 * w_2) \text{ ml/mg}$ and $A_2 = 0.0015$ where w_2 is weight percent butene comonomer, for all other ethylene polymers $dn/dc = 0.1048 \text{ ml/mg}$ and $A_2 = 0.0015$.

[0086] A high temperature viscometer, such as those made by Technologies, Inc. or Viscotek Corporation, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the equation $[\eta] = \eta_s/c$, where c is concentration and is determined from the IR5 broadband channel output. The viscosity MW at each point is calculated as $M = K_{PS} M^{\alpha_{PS}+1} / [\eta]$, where α_{PS} is 0.67 and K_{PS} is 0.000175. The average intrinsic viscosity, $\langle [\eta] \rangle$ of the sample is calculated by:

$$\langle[\eta]\rangle = \frac{\sum c_i[\eta]_i}{\sum c_i} \quad \text{EQ. 8}$$

where the summations are over the chromatographic slices, i , between the integration limits.

[0087] The long chain branching index (g'_{LCB} , also referred to as g'_{vis}) is defined as

$$g'_{LCB} = \frac{\langle[\eta]\rangle}{K\langle M_{IR} \rangle^\alpha} \quad \text{EQ. 9}$$

5 where $\langle M_{IR} \rangle$ is the viscosity average molecular weight calibrated with polystyrene standards, K and α are for the reference linear polymer, which are as calculated and published in literature (Sun, T. et al. Macromolecules 2001, 34, 6812), except that for purposes of this invention and claims thereto, $\alpha = 0.705$ and $K = 0.0002288$ for linear propylene polymers, $\alpha = 0.695$ and $K = 0.000181$ for linear butene polymers, α is 0.695 and K is 0.000579*(1-
10 0.0087*w2b+0.000018*(w2b)^2) for ethylene-butene copolymer where w2b is a bulk weight percent of butene comonomer, α is 0.695 and K is 0.000579*(1-0.0075*w2b) for ethylene-hexene copolymer where w2b is a bulk weight percent of hexene comonomer, and α is 0.695 and K is 0.000579*(1-0.0077*w2b) for ethylene-octene copolymer where w2b is a bulk weight percent of octene comonomer, and $\alpha = 0.695$ and $K = 0.0005$ for all other linear ethylene polymers.

15 **[0088]** Either the IR or LS detectors as noted above can be used for obtaining molecular weight values from GPC. The LS detector is used for molecular weight values noted herein, unless specifically noted otherwise as coming from the IR detector. However, we have also specifically noted in many instances the LS detector's use for molecular weight values — for example, a weight-average molecular weight determined using LS detector may be denoted as Mw (LS).
20 Furthermore, all comonomer wt%s as determined at specific molecular weight values (e.g., comonomer wt% at Mw, and/or at Mn, and/or at Mz) are determined based upon the molecular weight value as determined using LS detectors. Otherwise, where one sees Mz (IR), Mw (IR), etc., then the IR detector is used.

[0089] The TREF technique was performed as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., Vol. 20, pg. 441 (1982) and U.S. Pat. No. 5,008,204. which is incorporated by reference
25 herein. For the measurements, 0 C to 140 C temperature range was used for all samples with a crystallization ramp rate of 1 C/min and elution ramp rate of 2 C/min. The cumulative curve provides the wt % changes across the elution temperature range and also the wt % of high density (HD) from each of the samples.

30 **[0090]** Measurements for puncture peak force and puncture break energy at break can be measured using the procedure written in the standard test method of ASTM F1306. Specimens (6"

x 6”) are placed in the clamping apparatus. A probe is used to penetrate the film at a constant rate of 10 in/min. Minimum of 5 specimens are tested per sample.

[0091] Top load, Permanent set and retractive force at 50% recovery are determined as follows. Test samples measuring 50 mm×100 mm are stretched to 100% elongation at a speed of 500 mm/min. At 100% elongation, the samples are held for 1 second before being allowed to return to the starting position, also at a speed of 500 mm/min. The samples are held for 30 seconds, and the elongation cycle is repeated a second time. The test is conducted at 20° C. and 50% relative humidity. Permanent set is the increase in length, expressed as a percentage of the original length of the sample, by which the sample fails to return to its original length after each elongation cycle once the load is removed. For example, a permanent set of 0% means that after elongation the sample fully returns to its original length, while a permanent set of 100% means that the sample shows no elastic recovery at all after elongation. The top load (N) is the force at 100% elongation while Retractive force at 50% recovery is the force exerted by a sample at 50% elongation, measured as the sample retracts from 100% elongation and expressed in N. The values of top load (N), permanent set (%) and retractive force (N) are measured for both 1st and 2nd cycles from the test.

[0092] Izod impact strength is determined using the procedure based on ISO 180 method. All specimens are conditioned at the specified test temperature (-30 °C, -20 °C, 23 °C) for a minimum of four hours before testing. The impact resistance is reported in kJ/m². Charpy Impact test is performed based on the procedure in ISO 179 method and measures the resistance to impact from a pendulum. The specimen with 80 x 10 mm dimension is mounted horizontally and supported unclamped at both ends. The hammer is released and allowed to strike through the specimen. The impact energy absorbed in breaking the specimen at the cross sectional area behind the notch is expressed in kilojoules per square meter (kJ/m²). Specimens to be tested at sub-ambient temperatures (0°C, -20°C, -30°C and -40°C) must be conditioned at the requested temperature for a minimum of four hours in a sub-ambient chamber.

[0093] The Heat Deflection Temperature (°C) is based on the procedure outlined in ISO 75 method B and is the temperature at which a pre-deformation occurs at a specified load and temperature.

[0094] Flexural modulus is measured as per the procedure ISO 178 with a deformation rate @ 0.08 in/min. Dart Drop Impact Strength (DIS), reported in grams (g), (g/mil), or (g/μm) and measured as in accordance with ASTM D-1709, method A. The dart head is phenolic. It calculates

the impact failure weight, i.e., the weight for which 50% of the test specimens will fail under the impact.

[0095] Tear testing of films in the machine and transverse directions was conducted on a ProTear Elmendorf Tearing Tester using the ASTM D 1922–15 method. 10 specimens were tested and an average value in grams is reported from these measurements.

[0096] Haze was measured with HazeGard PLUS Hazemeter using method ASTM D1003. Haze is the percentage of transmitted light passing through the film that is deflected more than 2.5°. At least 3 film specimens are tested and average value (%) is reported from these measurements.

[0097] Heat seal initiation temperature can be measured by ASTM F1921. Heat seal initiation temperature is the temperature at which a heat seal forms immediately after the sealing operation, the strength of the heat seal being measured at a specified time interval (milliseconds) after completion of the sealing cycle and after the seal has cooled to ambient temperature and reached maximum strength. The strength of the seal is often specified – for example, the heat seal initiation temperature at 1 lb refers to the temperature at which a seal is formed that will have a strength of 1 lb force.

[0098] “Hot tack seal initiation temperature” is the temperature at which a heat seal forms immediately after the sealing operation, the strength of the heat seal being measured at a specified time interval (milliseconds) after completion of the sealing cycle and before the seal has cooled to ambient temperature and reached maximum strength. The strength of the seal is often specified – for example, the “heat seal initiation temperature at 2 N refers to the temperature at which a hot 2 N seal is formed. Hot tack seal initiation temperature can be measured by ASTM F1921.

[0099] Vicat softening temperature is measured using Ceast HDT 3 Vicat instrument. The specimens between 3mm and 6.5mm thick with at least 10mm square or 10mm in diameter are used. Three samples are conditioned in controlled temperature and humidity lab per ASTM D618 requirement ($23^{\circ}\pm 2^{\circ}\text{C}$ and $50\pm 10\%$) relative humidity. The Vicat temperature reported is the temperature at which a flat-ended needle of 1-mm² circular cross section penetrate a thermoplastic specimen to a depth of 1 mm under a 200 gm load perpendicular to the test specimen using a selected uniform rate of 50 C/hr.

Examples:

[00100] The foregoing discussion can be further described with reference to the following non-limiting examples. In the following examples, ethylene copolymers (“ECPs”) made from octene comonomer and having densities ranging from 0.850 g/cc and 0.902 g/cc and melt indexes ranging

from 0.3 to 200 MI were made according to the embodiments provided herein. The ECPs were compared to various commercially available EO copolymers with similar densities and MIs.

[00101] Comparative Example 1 (C1) is a Fortify C1055D ethylene octene copolymer from SABIC with a 0.857 g/cc density and a 1.0 g/10 min melt index

5 **[00102]** Comparative Example 2 (C2) is an ethylene octene copolymer from LGChem with a 0.857 g/cc density and a 1.0 g/10 min melt index

[00103] Comparative Example 3 (C3) is an Engage 8842 ethylene octene copolymer from The Dow chemical company with a 0.857 g/cc density and a 1.0 g/10 min melt index

[00104] Comparative Example 4 (C4) is a Queo 6201 ethylene octene copolymer from Borealis
10 with a 0.862 g/cc density and a 1.0 g/10 min melt index

[00105] Comparative Example 5 (C5) is an Engage 8100 ethylene octene copolymer from The Dow chemical company with a 0.870 g/cc density and a 1.0 g/10 min melt index

[00106] Comparative Example 6 (C6) is an Engage 8200 ethylene octene copolymer from The Dow chemical ethylene octene copolymer with a 0.870 g/cc density and a 5.0 g/10 min melt index

15 **[00107]** Comparative Example 7 (C7) is an Exact 5171 ethylene octene copolymer from ExxonMobil Chemical with a 0.868 g/cc density and a 1.0 g/10 min melt index

[00108] Comparative Example 8 (C8) is an Exact 5371 ethylene octene copolymer from ExxonMobil Chemical with a 0.868 g/cc density and a 5.0 g/10 min melt index

[00109] Comparative Example 9 (C9) is an Exact 5101 ethylene octene copolymer from
20 ExxonMobil Chemical with a 0.900 g/cc density and a 1.1 g/10 min melt index

[00110] Comparative Example 10 (C10) is an Affinity PL1880G ethylene octene copolymer from The Dow Chemical with a 0.902 g/cc density and 1.0 g/10 min melt index

[00111] ECPs S27-S31 were produced in a pilot sized solution reactor using di(para-triethylsilylphenyl)methylene (2,7-di-tertbutyl-fluorenyl) (cyclopentadienyl) hafnium dimethyl as the catalyst and N,N-dimethylanilinium-tetra(perfluoronaphthyl)borate as the co-catalyst/activator, both available from ExxonMobil Chemical Company. Table 1 shows the physical properties and molecular weights of the ECPs, as measured according to the test procedures described herein. Table 2 shows the physical properties and molecular weights of various comparative commercially available copolymers having similar density and MI.
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[00112] Table 1: physical properties and Mw of ethylene copolymers

ECPs	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/ Mn	Mz/ Mw	C8 wt%	Density (g/cc)	MI (g/ 10 min)
S1	26900	62800	112900	2.3	1.8	39.8	0.866	23.0
S2	37000	84900	151100	2.3	1.8	34.3	0.875	3.7
S3	27300	60300	104500	2.2	1.7	30.8	0.881	13.3
S4	39200	83600	152300	2.1	1.8	26.8	0.888	2.4
S5	42200	93600	170400	2.2	1.8	27.1	0.887	3.3
S6	23352	49245	81986	2.1	1.7	29.8	0.883	25
S7	14024	32055	55216	2.3	1.7	32.3	0.878	178
S8	25850	60671	110897	2.3	1.8	31.8	0.879	9.9
S9	21965	52577	94995	2.4	1.8	29.5	0.883	15.8
S10	29698	67547	121508	2.3	1.8	32.2	0.878	7.2
S11	24485	58666	113263	2.4	1.9	33.1	0.877	14
S12	23177	57034	118410	2.5	2.1	33.6	0.876	16
S13	31277	65329	109059	2.1	1.7	30.4	0.882	9
S14	45868	97531	166680	2.1	1.7	23.8	0.893	1.1
S15	39139	86896	151813	2.2	1.7	22.1	0.896	1.2
S16	38901	85853	149505	2.2	1.7	22.6	0.895	1.1
S17	39450	87133	150760	2.2	1.7	21.3	0.897	1.2
S18	36843	83766	148545	2.3	1.8	22.5	0.895	1.2
S19	37798	84390	149267	2.2	1.8	22.5	0.895	1.2
S20	37457	86643	154538	2.3	1.8	22.1	0.896	1.1
S21	30000	77927	159204	2.6	2.0	22.8	0.894	1.1
S22	34037	80145	147090	2.4	1.8	38.3	0.868	4.6
S23	45443	106643	195999	2.3	1.8	38.0	0.869	1.2
S24	49148	114334	209640	2.3	1.8	38.0	0.869	1.1
S25	48238	112233	203868	2.3	1.8	37.1	0.870	1.2
S26	35148	87867	166806	2.5	1.9	38.7	0.867	4.3
S27	66454	147004	257311	2.2	1.8	43.9	0.859	0.9
S28	49035	114949	210274	2.3	1.8	37.9	0.869	1.1
S29	52665	119291	211599	2.3	1.8	38.0	0.869	1.2

S30	55445	125644	224134	2.3	1.8	37.6	0.869	0.9
S31	58307	129837	227587	2.2	1.8	37.3	0.870	0.8

[00113] Table 2: physical properties and Mw of commercially available copolymers

Comp. Polymer	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mw	C8 wt%	Density (g/cc)	MI (g/ 10 min)
C1	62,540	157,841	297,822	2.5	1.9	44.6	0.857	1
C2	61,220	154,055	299,258	2.5	1.9	44.8	0.859	1.1
C3	69,234	147,339	261,416	2.1	1.8	43.9	0.862	1
C4	57,051	139,390	252,696	2.4	1.8	39.0	0.862	1
C5	60,476	128,256	219,206	2.1	1.7	34.7	0.870	1.1
C6	39,782	86,021	151,045	2.2	1.8	34.3	0.870	5
C7	54,277	118,101	206,173	2.2	1.7	34.9	0.868	1.1
C8	37,935	83,970	146,446	2.2	1.7	35.2	0.868	5
C9	38,286	83,658	144,738	2.2	1.7	17.9	0.900	1.1
C10	40,535	87,306	152,493	2.2	1.7	14.7	0.902	1.0

[00114] FIG. 1 shows the TREF composition curves for the lower density copolymers in Table 1, which were S27 and C3 (Engage 8842), C1 (Fortify C1055D) and C4 (Queo 6201). The comparative copolymers having densities ranging from (0.857 to 0.862 g/cc) had a single peak at the low elution temperature (0-30°C), whereas S27 (0.861 g/cc) had dominant peaks at the low elution temperature (0-30°C) as well as around 70°C. It was surprisingly discovered that the presence of this 70°C peak (0.1 to 5 wt% of the overall fraction) did not significantly change the molecular weight or the copolymer's other physical properties, namely, density, MI and Vicat softening temperature (39°C) equivalent to that for C2 (37°C) and C3 (41°C).

[00115] FIG. 2 shows the TREF composition curves from the mid-range density copolymers in Table 1, which were S22 and S31 and the comparative copolymers C5 (Engage 8100) and C6 (Engage 8200); C7 (Exact 5171) and C8 (Exact 5371). The comparative copolymers having densities ranging from (0.866 to 0.872 g/cc) had a single peak at the low elution temperature (0-30°C), whereas S22 and S31 (0.866 and 0.868 g/cc) both had dominant peaks at the low elution temperature (0-30°C) and also at around 70°C. The presence of this 70°C peak (0.1 to 5 wt%) of the overall fraction, also surprisingly, did not significantly change the molecular weight or the copolymer's other physical properties such as density, MI and Vicat softening temperature (49°C for S22 and 53°C for S31, 54°C for C7 and 51°C for C8).

[00116] FIG. 3 shows the TREF composition curves of the higher density copolymers (S14 and S21) in comparison to the commercially available C9 (Exact 5101) and C10 (Affinity PL1880G) having similar densities. As noted from the TREF composition curves in FIG. 3, ECPs S14 and S21 had two peaks: one at the lower elution temperature (higher C8 %) region and another at the higher elution temperature (70°C), whereas the comparative copolymers had only the single peak at the low elution temperature (0-30°C). Similar to S27, S22 and S31, the molecular weight nor density, MI and Vicat softening temperature were surprisingly changed.

[00117] FIG. 4 shows the TREF elution temperature peaks (Peak 1 and Peak 2) as a function of ethylene wt%. FIG. 5 shows the HD fraction (wt%) in the overall composition as a function of overall ethylene content (wt%) and can be seen to decrease with the increase in C2 wt% in the composition. This is likely promoted by a localized reaction region with relatively higher ethylene to co-monomer concentration ratio, and this region is likely near the feed make-up injection point.

Elasticity Performance

[00118] The elasticity performance of the lower density S27 was evaluated. Table 2 displays the elastic properties from hysteresis with 100 % elongation for the inventive lower density copolymer S27 in comparison to the similar density comparative example C3. As noted for the sample S27 with close to 5.5 wt% higher density fraction in the composition, elastic properties such as top load, retractive force and permanent set in both 1st and 2nd cycle were surprisingly equivalent to the comparative example C3 ethylene octene copolymer. This indicates the higher density fraction presence did not significantly alter the elastic performance of the resin.

[00119] Table 2. Elastic performance from hysteresis curves at 100 % elongation

Polymer	Top Load (N)	1st Retractive Force (N)	1st Permanent Set (%)	2nd Top Load (N)	2nd Retractive Force (N)	2nd Permanent Set (%)
C3	25.14	14.6	7.87	24.53	14.2	4.79
ECP S27	22.28	12.59	9.63	21.76	12.21	5.69

TPO Performance

[00120] Three of the foregoing ethylene copolymers ("ECP"), namely S22, S27, S31, were used to make TPO formulations of 20 wt% ECP, 20 wt% PP 7033, 50 wt% PP 7935, and 10 wt% talc. Table 3 below shows the low temperature (-20°C to 30°C) impact and flexural modulus of these TPO formulations in comparison to the comparative commercially available copolymers

with similar density and melt index. As reported in Table 3, the impact toughness values for the TPO formulation using the ECPs provided herein and having a high density fraction did not show significant deviation from the impact performance of the comparative examples. Besides the impact toughness, other mechanical properties such as flexural modulus and tensile strength showed equivalency while heat deflection temperature showed slightly better performance for the ECPs.

[00121] Table 3: TPO performance properties from the three lower density ECPs:

Polymer	MFR (g/10 min)	Flexural modulus (MPa)	Tensile strength (MPa)	Izod -20C (KJ/m2)	Izod -30C (KJ/m2)	Charpy - 20C (KJ/m2)	HDT (°C)
S22	17.8	1520	18.83	7.02	6.04	5.99	95.4
S27	19.7	1551	19.2	6.19	5.35	5.68	96.2
S31	21.6	1492	22.9	6.39	5.09	5.48	94.8
C5	17.2	1459	20.75	7.2	6.74	6.25	93.8
C7	17.9	1421	19.96	7.58	6.17	6.33	93.6
C6	22.5	1429	20.55	6.86	6.71	6.54	94.1
C8	21.9	1438	20.35	6.17	5.68	5.55	93.5
C3	18	1510	18.76	6.43	6.18	6.3	92.9

Film Performance

[00122] Two ECPs (S14 and S21) were made into blown films and tested for mechanical performance to test the effect, if any, due to the HD fraction. Table 4 reports the tests performed and results along with the extruder melt pressure and motor load. The properties of film are clearly related to the composition of the resin with different branching content as estimated by melt index ratio (I_{21}/I_2) and molecular weight distribution (M_w/M_n). The S14 ECP had a melt index ratio of 27 while S21 had a melt index ratio of 53. Properties of the films such as Dart impact, Machine direction tear, Puncture energy and haze higher for the inventive composition with lower MIR (less branching) were compared to the film with higher MIR (higher branching). The film with less branching showed better properties than film with higher branching while the processability as measured by melt pressure, motor load in the film line extruder shows opposite trend with MIR as expected.

[00123] Table 4 shows the sealing performance of monolayer blown film made from the ECPs at 0.894 g/cc density and 1.1 MI. Surprisingly, the presence of the higher density EO component

in ECPs S14 and S21 made no significant change to the sealing initiation or hot tack initiation temperatures.

[00124] Table 4. Blown Film properties.

	S14	S21	Exact 5101
Gauge (MIL)	1	1	1
MD Tear (gm)	91	39	68
Puncture energy at break [in-lb]	63	52	52
Dart A (g/mil)	603	267	391
Total Haze (%)	1.9	2.6	2.1
Seal Initiation Temperature @ 1 lb/in, °C	75	75	76
Hot Tack Initiation Temperature @ 2N/25.4 mm, °C	80	80	80
Motor Load [%]	62	46	58
Melt Pressure [2000-4000 PSI]	3960	3000	3992

5 Process Schematics

[00125] It is believed that higher catalyst to activator ratios during the process caused the creation of such compositions with two or three TREF peaks. FIG. 6 shows a schematic for making the ECPs described herein from a solution polymerization process with minor high density (HD) fractions. As depicted, the ethylene feed, catalyst and activator are typically present in the normal reactor feeds to the reactor system, while the “minor” feeds, with higher $C_2=/C_x=$ concentration ratios (Ethylene/Comonomer) can be injected into a conduit upstream of the reactor system, which does not mix instantaneously well when introduced to the bulk contents of the reactor system. As a result, a localized reaction, under higher $C_2=/C_x=$ concentration ratios, produce the HD fractions.

[00126] FIG. 7 shows the TREF high density fraction wt% versus the catalyst feeding rate relative to the activator, into the reactor. As shown in FIG. 7, a catalyst feed rate of > 2 cc/min generally led to a step increase in the HD fraction. It is believed that a higher catalyst to activator ratio promotes a localized reaction region with a relatively higher ethylene to co-monomer concentration ratio, and this region is likely near the feed make-up injection point.

[00127] FIG. 8 depicts an alternative schematic for solution polymerization for making copolymers having two or three TREF peaks. In this process, additional ethylene make-up is added downstream of the reactor system, prior to quench, to promote further polymerization reactions under higher $C_2=/C_x=$ ratio conditions, resulting in the HD fractions in the resulting composition.

Additional Embodiments

[00128] This disclosure may further include any one or more of the following non-limiting embodiments:

5 [00129] Embodiment 1: An ethylene copolymer, comprising: at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units from one or more C4 to C20 alpha olefins, wherein the copolymer has a density in the range of 0.850 g/cc to 0.915 g/cc; MI in the range of 0.1 dg/min to 1000 dg/min; MIR (I21.6 / I2.16) in the range of 18 to 100, and at least two TREF peaks, wherein at least one TREF peak is a major fraction that accounts for at least 90 wt% of the copolymer and wherein at least one TREF peak is a minor fraction that accounts for less
10 than 8 wt% of the copolymer and is found in the range of 60°C to 95°C.

[00130] Embodiment 2: The ethylene copolymer of embodiment 1, wherein the major fraction TREF peak is found in the range of 0°C to 80°C.

[00131] Embodiment 3: The ethylene copolymer of embodiments 1 or 2, wherein the copolymer is polymerized in a solution polymerization process with a plug flow reactor or CSTR
15 and has a cement concentration (weight polymer / weight solvent) of 6% to 40%.

[00132] Embodiment 4: The ethylene copolymer of any embodiment 1 to 3, wherein the copolymer has a MWD (Mw/Mn) of from 1.2 to 5.0.

[00133] Embodiment 5: The ethylene copolymer of any embodiment 1 to 4, wherein the copolymer has a long branching index as measured from GPC-4D from 0.850 to 0.990.

20 [00134] Embodiment 6: The ethylene copolymer of any embodiment 1 to 5, wherein the copolymer is used in, TPO, injection molding, elastic and film applications.

[00135] Embodiment 7: The ethylene copolymer of any embodiment 1 to 6, wherein the copolymer is polymerized in a single reactor using a single metallocene catalyst system.

[00136] Embodiment 8: The ethylene copolymer of any embodiment 1 to 7, wherein the
25 copolymer further comprises one or more pellet coating additives.

[00137] Embodiment 9: The ethylene copolymer of any embodiment 1 to 8, wherein the copolymer has no added metal stearates or siloxanes.

[00138] Embodiment 10: The ethylene copolymer of any embodiment 1 to 9, wherein the copolymer has no added HDPE, LDPE or talc dusting agents.

30 [00139] Embodiment 11: A method for making a copolymer by solution polymerization comprising: (a) feeding ethylene, at least one comonomer, and a solvent in controlled proportions to a conduit upstream of a solution polymerization reactor; (b) adding a single metallocene catalyst and an activator to the conduit; (c) polymerizing at least a portion of the ethylene and the at least

one other monomer in the solution polymerization reactor to produce an ethylene pre-polymer having at least 5 wt% of the comonomer; (d) feeding the ethylene pre-polymer to the solution polymerization reactor; (e) feeding additional ethylene, comonomer, catalyst and activator in controlled proportions to the solution polymerization reactor and optionally additional solvent; and (f) operating the solution polymerization reactor to produce an ethylene copolymer comprising: at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units from one or more C4 to C20 alpha olefins; a density in the range of 0.850 g/cc to 0.915 g/cc; MI in the range of 0.1 dg/min to 1000 dg/min; MIR ($I_{21.6} / I_{2.16}$) in the range of 18 to 100, and at least two TREF peaks, wherein at least one TREF peak is a major fraction that accounts for at least 90 wt% of the ethylene copolymer and wherein at least one TREF peak is a minor fraction that accounts for less than 8 wt% of the ethylene copolymer and is found in the range of 60°C to 95°C.

[00140] Embodiment 12: The method of embodiment 11, wherein 5-45 wt % of the total amount of catalyst and activator is added to the conduit upstream of the solution polymerization reactor.

[00141] Embodiment 13: The method of embodiments 11 or 12, wherein 5-45 wt % of the total amount of ethylene is added to the conduit upstream of the solution polymerization reactor.

[00142] Embodiment 14: The method of any embodiment 11 to 13, wherein 5-45 wt % of the total amount of comonomer is added to the conduit upstream of the solution polymerization reactor.

[00143] Embodiment 15: The method of any embodiment 11 to 14, wherein at least 90 wt % of the ethylene copolymer is made in the solution polymerization reactor and the balance of the ethylene copolymer made in the conduit upstream of the solution polymerization reactor.

[00144] Embodiment 16: A method for making a copolymer by solution polymerization comprising: (a) feeding ethylene, at least one comonomer, and a solvent in controlled proportions to a solution polymerization reactor; (b) adding a single metallocene catalyst and an activator to the solution polymerization reactor; (c) polymerizing at least a portion of the ethylene and the at least one other monomer in the solution polymerization reactor to produce an ethylene copolymer having at least 5 wt% of the comonomer; (d) flowing the ethylene pre-polymer from the solution polymerization reactor; (e) feeding additional ethylene in controlled proportions to the ethylene copolymer within a conduit downstream of the solution polymerization reactor to provide an ethylene copolymer product comprising: at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units from one or more C4 to C20 alpha olefins; a density in the range of

0.850 g/cc to 0.915 g/cc; MI in the range of 0.1 dg/min to 1000 dg/min; MIR (I21.6 / I2.16) in the range of 18 to 100, and at least two TREF peaks, wherein at least one TREF peak is a major fraction that accounts for at least 90 wt% of the ethylene copolymer product and wherein at least one TREF peak is a minor fraction that accounts for less than 8 wt% of the ethylene copolymer product and is found in the range of 60°C to 95°C.

[00145] Embodiment 17: The method of embodiment 16, wherein 5-45 wt % of the total amount of catalyst and activator is added to the conduit downstream of the solution polymerization reactor.

[00146] Embodiment 18: The method of embodiments 16 or 17, wherein 5-45 wt % of the total amount of ethylene is added to the conduit downstream of the solution polymerization reactor.

[00147] Embodiment 19: The method of any embodiment 16 to 18, wherein 5-45 wt % of the total amount of comonomer is added to the conduit downstream of the solution polymerization reactor.

[00148] Embodiment 20: The method of any embodiment 16 to 19, wherein at least 90 wt % of the ethylene copolymer is made in the solution polymerization reactor and the balance of the ethylene copolymer made in the conduit downstream of the solution polymerization reactor.

[00149] All numerical values are "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[00150] Many alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure and that when numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[00151] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[00152] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

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CLAIMS:*What is claimed is:*

1. An ethylene copolymer, comprising:
at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units
5 from one or more C4 to C20 alpha olefins, wherein the copolymer has:
a density in the range of 0.850 g/cc to 0.915 g/cc;
MI in the range of 0.1 dg/min to 1000 dg/min;
MIR ($I_{21.6} / I_{2.16}$) in the range of 18 to 100, and
at least two TREF peaks, wherein at least one TREF peak is a major fraction that
10 accounts for at least 90 wt% of the copolymer and wherein at least one TREF peak is a minor
fraction that accounts for less than 8 wt% of the copolymer and is found in the range of 60°C
to 95°C.
2. The ethylene copolymer of claim 1, wherein the major fraction TREF peak is found in
15 the range of 0°C to 80°C.
3. The ethylene copolymer of claim 1, wherein the copolymer is polymerized in a solution
polymerization process with a plug flow reactor or CSTR and has a cement concentration
(weight polymer / weight solvent) of 6% to 40%.
- 20 4. The ethylene copolymer of claim 1, wherein the copolymer has a MWD (M_w/M_n) of
from 1.2 to 5.0.
5. The ethylene copolymer of claim 1, wherein the copolymer has a long branching index
25 as measured from GPC-4D from 0.850 to 0.990.
6. The ethylene copolymer of claim 1, wherein the copolymer is used in, TPO, injection
molding, elastic and film applications.
- 30 7. The ethylene copolymer of claim 1, wherein the copolymer is polymerized in a single
reactor using a single metallocene catalyst system.

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8. The ethylene copolymer of claim 1, wherein the copolymer further comprises one or more pellet coating additives.
9. The ethylene copolymer of claim 1, wherein the copolymer has no added metal stearates
5 or siloxanes.
10. The ethylene copolymer of claim 1, wherein the copolymer has no added HDPE, LDPE or talc dusting agents.
- 10 11. A method for making a copolymer by solution polymerization comprising:
(a) feeding ethylene, at least one comonomer, and a solvent in controlled proportions to a conduit upstream of a solution polymerization reactor;
(b) adding a single metallocene catalyst and an activator to the conduit;
(c) polymerizing at least a portion of the ethylene and the at least one other monomer
15 in the solution polymerization reactor to produce an ethylene pre-polymer having at least 5 wt% of the comonomer;
(d) feeding the ethylene pre-polymer to the solution polymerization reactor;
(e) feeding additional ethylene, comonomer, catalyst and activator in controlled proportions to the solution polymerization reactor and optionally additional solvent; and
20 (f) operating the solution polymerization reactor to produce an ethylene copolymer comprising:
at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units from one or more C4 to C20 alpha olefins;
a density in the range of 0.850 g/cc to 0.915 g/cc;
25 MI in the range of 0.1 dg/min to 1000 dg/min;
MIR ($I_{21.6} / I_{2.16}$) in the range of 18 to 100, and
at least two TREF peaks, wherein at least one TREF peak is a major fraction that accounts for at least 90 wt% of the ethylene copolymer and wherein at least one TREF peak is a minor fraction that accounts for less than 8 wt% of the ethylene
30 copolymer and is found in the range of 60°C to 95°C.
12. The method of claim 11, wherein 5-45 wt % of the total amount of catalyst and activator is added to the conduit upstream of the solution polymerization reactor.

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13. The method of claim 11, wherein 5-45 wt % of the total amount of ethylene is added to the conduit upstream of the solution polymerization reactor.

5 14. The method of claim 11, wherein 5-45 wt % of the total amount of comonomer is added to the conduit upstream of the solution polymerization reactor.

15. The method of claim 11, wherein at least 90 wt % of the ethylene copolymer is made in the solution polymerization reactor and the balance of the ethylene copolymer made in the
10 conduit upstream of the solution polymerization reactor.

16. A method for making a copolymer by solution polymerization comprising:

(a) feeding ethylene, at least one comonomer, and a solvent in controlled proportions to a solution polymerization reactor;

15 (b) adding a single metallocene catalyst and an activator to the solution polymerization reactor;

(c) polymerizing at least a portion of the ethylene and the at least one other monomer in the solution polymerization reactor to produce an ethylene copolymer having at least 5 wt% of the comonomer;

20 (d) flowing the ethylene pre-polymer from the solution polymerization reactor;

(e) feeding additional ethylene in controlled proportions to the ethylene copolymer within a conduit downstream of the solution polymerization reactor to provide an ethylene copolymer product comprising:

25 at least 60 wt% of ethylene derived units and 10-40 wt% of comonomer derived units from one or more C4 to C20 alpha olefins;

a density in the range of 0.850 g/cc to 0.915 g/cc;

MI in the range of 0.1 dg/min to 1000 dg/min;

MIR ($I_{21.6} / I_{2.16}$) in the range of 18 to 100, and

30 at least two TREF peaks, wherein at least one TREF peak is a major fraction that accounts for at least 90 wt% of the ethylene copolymer product and wherein at least one TREF peak is a minor fraction that accounts for less than 8 wt% of the ethylene copolymer product and is found in the range of 60°C to 95°C.

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17. The method of claim 16, wherein 5-45 wt % of the total amount of catalyst and activator is added to the conduit downstream of the solution polymerization reactor.

18. The method of claim 16, wherein 5-45 wt % of the total amount of ethylene is added
5 to the conduit downstream of the solution polymerization reactor.

19. The method of claim 16, wherein 5-45 wt % of the total amount of comonomer is added to the conduit downstream of the solution polymerization reactor.

10 20. The method of claim 16, wherein at least 90 wt % of the ethylene copolymer is made in the solution polymerization reactor and the balance of the ethylene copolymer made in the conduit downstream of the solution polymerization reactor.