

MULTIMODAL ETHYLENE-BASED COPOLYMER COMPOSITIONS AND PROCESSES OF PRODUCING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/295,182 filed December 30, 2021, the entire disclosure of which is hereby incorporated herein by reference.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to polymer compositions and more specifically relate to multimodal ethylene-based copolymer compositions and processes of producing the same.

BACKGROUND

[0003] The use of polyolefin compositions in industries such as packaging applications is generally known. A variety of conventional methods may be employed to produce such polyolefin compositions. Various polymerization techniques using different catalyst systems have been employed to produce such polyolefin compositions suitable for packaging applications. However, despite the research efforts in developing compositions suitable for, in some embodiments, packaging applications, there is still a need for improved polyethylene compositions suitable for packaging applications that may have a good balance of physical properties and melt strength at desired polymer composition densities.

SUMMARY

[0004] Melt strength and processability are correlated properties of polyethylene resins. In general, a higher melt strength provides for a polyethylene resin with improved processability.

[0005] Additionally, conventional polyethylene resins produced by conventional processes typically see a tradeoff between the resin's mechanical properties and melt strength. For example, conventional radical processes produce low density polyethylenes (LDPE) that typically exhibit high melt strength but have poor mechanical properties. In contrast, linear low-density

polyethylenes (LLDPE) made via solution or gas phase processes typically have poor melt strength but excellent mechanical properties.

[0006] Therefore, to increase processability, some amount of LDPE may typically be blended with LLDPE in order to improve the processability and melt strength of LLDPE resins. Unfortunately, the addition of LDPE leads to decreased the mechanical properties of the resulting blends when compared with pure LLDPE resin.

[0007] Accordingly, there are needs for solution polymerization processes that produce polyethylene resins that may have melt strengths comparable to polyethylene resins produced via a radical process. Due to the potential hazards associated with radical polymerization on an industrial scale, there are needs for solution polymerization processes that produce polyethylene resins that may have melt strengths comparable to LDPE resins produced via a radical process.

[0008] Embodiments of the present disclosure meet those needs by providing multimodal ethylene-based copolymers that comprise a bulk low molecular weight (LMW) ethylene-based component made by one catalyst or catalysts and a high molecular weight (HMW) ethylene-based component made by a different catalyst or catalysts.

[0009] The multimodal ethylene-based copolymers described herein may possess long chain branching that, along with the HMW ethylene-based component, allows for melt strengths to be achieved that are comparable to or higher than various LDPEs produced via conventional processes.

[0010] Embodiments of this disclosure include processes of making a multimodal ethylene-based copolymer. In embodiments, the process of polymerizing a multi-modal polyethylene polymer includes contacting ethylene and optionally one or more α -olefin monomers with at least two catalyst systems in a solution reactor at a reactor temperature of greater than 150°C. The at least two catalyst systems produce a vinyl end group count per 1000 carbon atoms that is greater than 0.3, wherein the vinyl end group count per 1000 carbon atoms is measured by 600 MHz nuclear magnetic resonance (NMR) instrument. A first catalyst system of the at least two catalyst systems comprises a first procatalyst; and a second catalyst system of the at least two catalyst systems comprises a second procatalyst having a reactivity ratio of less than 20, wherein the reactivity ratio of the first procatalyst is measured in a single reactor with only the first catalyst

system in the presence of 1250 grams of ISOPAR-E with a mol fraction of ethylene in solution of 0.709 at a reactor temperature of at least 150°C. In some embodiments, the multi-modal polyethylene polymer at least 10% weight fraction greater than 500 kg/mol.

DETAILED DESCRIPTION

[0011] Embodiments of multimodal ethylene-based copolymer compositions and processes of producing the same will now be described. The ethylene-based polymers, of ethylene and optionally one or more co-monomers such as α -olefins, may comprise from at least 50 mole percent (mol%) monomer units derived from ethylene. All individual values and subranges encompassed by “from at least 50 mole percent” are disclosed herein as separate embodiments; for example, the ethylene based polymers may comprise at least 60 mole percent monomer units derived from ethylene; at least 70 mole percent monomer units derived from ethylene; at least 80 mole percent monomer units derived from ethylene; or from 50 to 100 mole percent monomer units derived from ethylene; or from 80 to 100 mole percent monomer units derived from ethylene.

[0012] Processes

[0013] In embodiments, the process of polymerizing a multi-modal polyethylene polymer includes contacting ethylene and optionally one or more α -olefin monomers with at least two catalyst systems in a solution reactor at a reactor temperature of greater than 150°C. The at least two catalyst systems produce a vinyl end group count per 1000 carbon atoms is greater than 0.3, wherein the vinyl end group count per 1000 carbon atoms is measured by 600 MHz nuclear magnetic resonance (NMR) instrument. A first catalyst system of the at least two catalyst systems comprises a first procatalyst; and a second catalyst system of the at least two catalyst systems comprises a second procatalyst having a reactivity ratio of less than 20, wherein the reactivity ratio of the first procatalyst is measured in a single reactor with only the first catalyst system in the presence of 1250 grams of ISOPAR-E with a mol fraction of ethylene in solution of 0.709 at a reactor temperature of at least 150°C. In some embodiments, the multi-modal polyethylene polymer at least 10% weight fraction greater than 500 kg/mol.

[0014] In embodiments, the solution polymerization reactor system may include one or more reactors. In embodiments, the solution polymerization reactor system may be a single reactor system. In embodiments, the solution polymerization reactor system may be a dual reactor system.

In embodiments that comprise a dual reactor system, the solution polymerization reactor system may include a first reactor and a second reactor, in which the first reactor and the second reactor may have varying order. For example, the second reactor may be down stream of the first reactor. However, the converse is also contemplated. Such solution polymerization processes include using one or more conventional reactors such as loop reactors, isothermal reactors, adiabatic reactors, fluidized bed gas phase reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[0015] In embodiments, the at least two catalyst systems are in one reactor vessel. A single reactor has one reactor vessel and dual reactor had two reactor vessels.

[0016] In one or more embodiments, when the solution reactor is a single reactor, the at least two catalyst systems include a first catalyst system and a second catalyst system. In some embodiments, when the solution reactor is a dual reactor, the first catalyst system and the second catalyst system are in a first reactor of the dual reactors and the second reactor of the dual reactor includes a third catalyst system. In various embodiments, when the solution reactor is a dual reactor, the first catalyst system and the second catalyst system may be in one reactor of the dual reactors and the other reactor of the dual reactor includes a third catalyst system. In other embodiments, when the solution reactor is a dual reactor, the first catalyst system may be in one reactor of the dual reactors and the other reactor of the dual reactor includes a second catalyst system and a third catalyst system.

[0017] In embodiments, the first catalyst system includes a reaction product a first procatalyst and an activator; the second catalyst system comprises a reaction product a second procatalyst and an activator, and a third catalyst system comprises a reaction product a third procatalyst and an activator. In some embodiments, the activator in each catalyst system is the same. In other embodiments, the activator in each catalyst system is not the same. In various embodiments, the activator is in the first catalyst system and the second catalyst system is the same and different in the third catalyst system. In some embodiments, the activator in the first catalyst system is different than the activator in the second catalyst system.

[0018] In one or more embodiments, the first procatalyst is different from the second procatalyst and the second procatalyst is different from the third procatalyst. In various embodiments, the first procatalyst is different from the third procatalyst.

[0019] In one or more embodiments, the at least two catalyst systems produce a vinyl end group count per 1000 carbon atoms is greater than 0.4 or greater than 0.45, wherein the vinyl end group count per 1000 carbon atoms is measured by 600 MHz nuclear magnetic resonance (NMR) instrument. The phrase the “vinyl end group count per 1000 carbon atoms” means the number of vinyl (carbon-carbon double bonds) groups in a reactor solution at 600 MHz nuclear magnetic resonance (NMR) instrument.

[0020] The multimodal polyethylene-based compositions of this disclosure have an increased melt strength in comparison to typical LLDPE compositions and superior mechanical properties to typical LDPE compositions. Without intent to be bound by theory, it is believed that one of the at least two catalyst systems in the multimodal polyethylene-based composition creates a high molecular weight fraction. At least one of the catalysts in the first, second, and optionally third catalyst systems, or a combination of catalyst systems, produce a vinyl end group count per 1000 carbon atoms of greater than 0.3, greater than 0.4, or greater than 0.45. Some of the vinyl end groups produced by at least one of the at least two catalyst systems may be reinserted into the polymer chain to create long chain branches, and some of the vinyl groups will remain in the final composition. The combination of the long chain branches and the high molecular weight fraction increases the melt strength of the polymer of the inventive examples.

[0021] In embodiments, the multimodal ethylene-based copolymer compositions may be produced via a solution polymerization process. In embodiments, the process of making a multimodal ethylene-based copolymer may include contacting at least two α -olefin monomers in the presence of a catalyst system comprising at least one low molecular weight catalyst and at least one high molecular weight catalyst in the solution polymerization reactor system.

[0022] In embodiments, ethylene and at least one α -olefin monomer may be polymerized in the presence of a catalyst to produce the multimodal ethylene-based copolymer compositions described herein. Typically, the α -olefin monomers have no more than 20 carbon atoms. For example, the α -olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α -olefin co-monomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. For example, the one or more α -olefin co-monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene.

In some embodiments, the α -olefin is not a diene. In embodiments, the α -olefin co-monomers and the process solvent may be purified with molecular sieves before introduction into the solution polymerization reactor system. The solvent, monomer, comonomers, and hydrogen may be combined and feed to the solution polymerization reactor system. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR E from ExxonMobil Chemical. In embodiments, the combined feed may be temperature controlled to a temperature of from 5 °C to 50 °C, from 5 °C to 25 °C, from 5 °C to 10 °C, from 10 °C to 50 °C, from 10 °C to 25 °C, or from 25 °C to 50 °C.

[0023] The catalyst systems, described in the subsequent section in more detail, are utilized in the polymerization of olefins to produce the multimodal ethylene-based copolymer compositions described herein. As stated previously, the catalyst system in the solution polymerization reactor system may comprise at least one first catalyst that produces a high molecular weight (HMW) ethylene-based component and at least one second catalyst that produces a bulk low molecular weight (LMW) ethylene-based component. The term “bulk” in reference to “bulk low molecular weight” means greater than 50 weight percent of the total composition.

[0024] In one embodiment, the multimodal ethylene-based copolymer composition may be produced, via a solution polymerization process, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of a first catalyst to produce the high molecular weight (HMW) ethylene-based component. In one or more embodiments, the first catalyst may have a first efficiency of from 1,000 kg polymer/g metal to 30,000 kg polymer/g metal. In further embodiments, the first catalyst may have a first efficiency of from 1,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 20,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 15,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 10,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 5,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 20,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 15,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 10,000 kg polymer/g metal, from 10,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 10,000 kg polymer/g metal to 20,000 kg polymer/g metal, from 10,000 kg polymer/g metal to 15,000 kg polymer/g metal, from 15,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 15,000 kg polymer/g metal to 20,000 kg polymer/g metal, or from 1,000

kg polymer/g metal to 25,000 kg polymer/g metal. In one or more embodiments, the first catalyst may exhibit a first reactivity ratio of less than 20. In further embodiments, the first catalyst may exhibit a first reactivity ratio of less than 20, less than 15, or less than 10. In further embodiments, the first catalyst may exhibit a first reactivity ratio of from 10 to 20, from 10 to 15, or from 15 to 20.

[0025] In one embodiment, the multimodal ethylene-based copolymer composition may be produced, via a solution polymerization process, wherein ethylene, and optionally one or more α -olefins, are polymerized in the presence of a second catalyst to produce a bulk low molecular weight (LMW) ethylene-based component. In one or more embodiments, the second catalyst may have a second catalyst efficiency of from 1,000 kg polymer/g metal to 30,000 kg polymer/g metal. In further embodiments, the second catalyst may have a low molecular weight catalyst efficiency of from 1,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 20,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 15,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 10,000 kg polymer/g metal, from 1,000 kg polymer/g metal to 5,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 20,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 15,000 kg polymer/g metal, from 5,000 kg polymer/g metal to 10,000 kg polymer/g metal, from 10,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 10,000 kg polymer/g metal to 20,000 kg polymer/g metal, from 10,000 kg polymer/g metal to 15,000 kg polymer/g metal, from 15,000 kg polymer/g metal to 25,000 kg polymer/g metal, from 15,000 kg polymer/g metal to 20,000 kg polymer/g metal, or from 1,000 kg polymer/g metal to 25,000 kg polymer/g metal.

[0026] In one embodiment, the multimodal ethylene-based copolymer composition may be produced, via a solution polymerization process, in a dual reactor system, for example a dual loop reactor system, wherein ethylene, and optionally one or more α -olefins, are polymerized in the presence of the low molecular weight catalyst system, in a first reactor, to produce the bulk low molecular weight (LMW) ethylene-based component and ethylene, and optionally one or more α -olefins, are polymerized in the presence of the high molecular weight catalyst system, in a second reactor, to produce the high molecular weight ethylene-based component. Additionally, one or more cocatalysts may be present. In another embodiment, the multimodal ethylene-based copolymer composition may be produced via a solution polymerization process, in a single reactor system, for example, a single loop reactor system, wherein ethylene, and optionally one or more

α -olefins, are polymerized in the presence of the low molecular weight catalyst system and the high molecular weight catalyst system. Additionally, one or more cocatalysts may be present.

[0027] In embodiments, the solution polymerization reactor system may include one or more reactors that operate at a temperature greater than 150 °C. In embodiments, the solution polymerization reactor system may include one or more reactors that operate at a temperature from 160 °C to 200 °C, from 160 °C to 190 °C, from 160 °C to 180 °C, from 160 °C to 170 °C, from 170 °C to 200 °C, from 170 °C to 190 °C, from 170 °C to 180 °C, from 180 °C to 200 °C, from 180 °C to 190 °C, or from 190 °C to 200 °C. Further improvements to solution polymerization systems involving multicatalyst systems making high melt strength polyethylene can be made. One improvement to said process would be to operate at elevated reactor temperatures (> 150 °C), which would increase production rate and decrease energy consumption while still producing the desirable polyethylene product with commercially acceptable catalyst efficiency and process control. Such an improvement has not been demonstrated in the state of the art.

[0028] The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to above reaction pressure at 525 psig. The solvent and comonomer (1-octene) feeds are pressurized via mechanical positive displacement pump to above reaction pressure at 525 psig.

[0029] Immediately following each fresh injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The effluent from the polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits the first reactor loop and passes through a control valve (responsible for maintaining the pressure of the first reactor at a specified target). As the stream exits the reactor it is contacted with water to stop the reaction. In addition, various additives such as antioxidants, could be added at this point. The stream then went through another set of static mixing elements to evenly disperse the catalyst kill and additives.

[0030] Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passed through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower boiling reaction components. The stream then enters a two-stage separation and devolatilization system where the polymer is removed from the solvent, hydrogen, and unreacted monomer and

comonomer. The separated and devolatilized polymer melt is pumped through a die specially designed for underwater pelletization, cut into uniform solid pellets, dried, and transferred into a box for storage.

[0031] Catalyst Systems

[0032] Specific embodiments of catalyst systems that can, in one or more embodiments, be used to produce the multimodal ethylene-based copolymer compositions described herein will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, 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.

[0033] The term “independently selected” is used herein to indicate that the R groups, such as, R¹, R², R³, R⁴, and R⁵ can be identical or different (e.g., R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc.). Use of the singular includes use of the plural and vice versa (e.g., a hexane solvent, includes hexanes). A named R group will generally have the structure that is recognized in the art as corresponding to R groups having that name. These definitions are intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

[0034] The term “procatalyst” refers to a compound that has catalytic activity when combined with an activator. The term “activator” refers to a compound that chemically reacts with a procatalyst in a manner that converts the procatalyst to a catalytically active catalyst. As used herein, the terms “co-catalyst” and “activator” are interchangeable terms.

[0035] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₄₀)alkyl is an alkyl group having from 1 to 40 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S. An R^S substituted version of a chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–C₄₀)alkyl substituted with exactly one group R^S, where R^S is

phenyl ($-\text{C}_6\text{H}_5$)” may contain from 7 to 46 carbon atoms. Thus, in general when a chemical group defined using the “($\text{C}_x\text{--}\text{C}_y$)” parenthetical is substituted by one or more carbon atom-containing substituents R^{S} , the minimum and maximum total number of carbon atoms of the chemical group is determined by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^{S} .

[0036] The term “substitution” means that at least one hydrogen atom ($-\text{H}$) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or function group is replaced by a substituent (e.g., R^{S}). The term “persubstitution” means that every hydrogen atom (H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^{S}). The term “polysubstitution” means that at least two, but fewer than all, hydrogen atoms bonded to carbon atoms or heteroatoms of a corresponding unsubstituted compound or functional group are replaced by a substituent.

[0037] The term “ $-\text{H}$ ” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “ $-\text{H}$ ” are interchangeable, and unless clearly specified mean the same thing.

[0038] The term “($\text{C}_1\text{--}\text{C}_{40}$)hydrocarbyl” means a hydrocarbon radical of from 1 to 40 carbon atoms and the term “($\text{C}_1\text{--}\text{C}_{40}$)hydrocarbylene” means a hydrocarbon diradical of from 1 to 40 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic, including bicyclic; 3 carbon atoms or more) or acyclic and is unsubstituted or substituted by one or more R^{S} .

[0039] In this disclosure, a ($\text{C}_1\text{--}\text{C}_{40}$)hydrocarbyl can be an unsubstituted or substituted ($\text{C}_1\text{--}\text{C}_{40}$)alkyl, ($\text{C}_3\text{--}\text{C}_{40}$)cycloalkyl, ($\text{C}_3\text{--}\text{C}_{20}$)cycloalkyl- $(\text{C}_1\text{--}\text{C}_{20})$ alkylene, ($\text{C}_6\text{--}\text{C}_{40}$)aryl, or ($\text{C}_6\text{--}\text{C}_{20}$)aryl- $(\text{C}_1\text{--}\text{C}_{20})$ alkylene. In some embodiments, each of the aforementioned ($\text{C}_1\text{--}\text{C}_{40}$)hydrocarbyl groups has a maximum of 20 carbon atoms (i.e., ($\text{C}_1\text{--}\text{C}_{20}$)hydrocarbyl) and embodiments, a maximum of 12 carbon atoms.

[0040] The terms “($\text{C}_1\text{--}\text{C}_{40}$)alkyl” and “($\text{C}_1\text{--}\text{C}_{18}$)alkyl” mean a saturated straight or branched hydrocarbon radical of from 1 to 40 carbon atoms or from 1 to 18 carbon atoms, respectively, that is unsubstituted or substituted by one or more R^{S} . Examples of unsubstituted ($\text{C}_1\text{--}\text{C}_{40}$)alkyl are unsubstituted ($\text{C}_1\text{--}\text{C}_{20}$)alkyl; unsubstituted ($\text{C}_1\text{--}\text{C}_{10}$)alkyl; unsubstituted ($\text{C}_1\text{--}\text{C}_5$)alkyl; methyl;

ethyl; 1-propyl; 2-propyl; 1-butyl; 2-butyl; 2-methylpropyl; 1,1-dimethylethyl; 1-pentyl; 1-hexyl; 1-heptyl; 1-nonyl; and 1-decyl. Examples of substituted (C₁–C₄₀)alkyl are substituted (C₁–C₂₀)alkyl, substituted (C₁–C₁₀)alkyl, trifluoromethyl, and [C₄₅]alkyl. The term “[C₄₅]alkyl” (with square brackets) means there is a maximum of 45 carbon atoms in the radical, including substituents, and is, for example, a (C₂₇–C₄₀)alkyl substituted by one R^S, which is a (C₁–C₅)alkyl, respectively. Each (C₁–C₅)alkyl may be methyl, trifluoromethyl, ethyl, 1-propyl, 1-methylethyl, or 1,1-dimethylethyl.

[0041] The term “(C₆–C₄₀)aryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic aromatic hydrocarbon radical of from 6 to 40 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms, and the mono-, bi- or tricyclic radical comprises 1, 2, or 3 rings, respectively; wherein the 1 ring is aromatic and the 2 or 3 rings independently are fused or non-fused and at least one of the 2 or 3 rings is aromatic. Examples of unsubstituted (C₆–C₄₀)aryl are unsubstituted (C₆–C₂₀)aryl unsubstituted (C₆–C₁₈)aryl; 2-(C₁–C₅)alkyl-phenyl; 2,4-bis(C₁–C₅)alkyl-phenyl; phenyl; fluorenyl; tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; and phenanthrene. Examples of substituted (C₆–C₄₀)aryl are substituted (C₁–C₂₀)aryl; substituted (C₆–C₁₈)aryl; 2,4-bis[(C₂₀)alkyl]-phenyl; polyfluorophenyl; pentafluorophenyl; and fluoren-9-one-1-yl.

[0042] The term “(C₃–C₄₀)cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 40 carbon atoms that is unsubstituted or substituted by one or more R^S. Other cycloalkyl groups (e.g., (C_x–C_y)cycloalkyl) are defined in an analogous manner as having from x to y carbon atoms and being either unsubstituted or substituted with one or more R^S. Examples of unsubstituted (C₃–C₄₀)cycloalkyl are unsubstituted (C₃–C₂₀)cycloalkyl, unsubstituted (C₃–C₁₀)cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C₃–C₄₀)cycloalkyl are substituted (C₃–C₂₀)cycloalkyl, substituted (C₃–C₁₀)cycloalkyl, cyclopentanone-2-yl, and 1-fluorocyclohexyl.

[0043] Examples of (C₁–C₄₀)hydrocarbylene include unsubstituted or substituted (C₆–C₄₀)arylene, (C₃–C₄₀)cycloalkylene, and (C₁–C₄₀)alkylene (e.g., (C₁–C₂₀)alkylene). In some embodiments, the diradicals are on the same carbon atom (e.g., –CH₂–) or on adjacent carbon atoms (i.e., 1,2- diradicals), or are spaced apart by one, two, or more than two intervening carbon atoms (e.g., respective 1,3-diradicals, 1,4-diradicals, etc.). Some diradicals include α,ω -diradical.

The α,ω -diradical is a diradical that has maximum carbon backbone spacing between the radical carbons. Some examples of (C₂–C₂₀)alkylene α,ω -diradicals include ethan-1,2-diyl (i.e. –CH₂CH₂–), propan-1,3-diyl (i.e. –CH₂CH₂CH₂–), 2-methylpropan-1,3-diyl (i.e. –CH₂CH(CH₃)CH₂–). Some examples of (C₆–C₅₀)arylene α,ω -diradicals include phenyl-1,4-diyl, naphthalen-2,6-diyl, or naphthalen-3,7-diyl.

[0044] The term “(C₁–C₄₀)alkylene” means a saturated straight chain or branched chain diradical (i.e., the radicals are not on ring atoms) of from 1 to 40 carbon atoms that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted (C₁–C₅₀)alkylene are unsubstituted (C₁–C₂₀)alkylene, including unsubstituted –CH₂CH₂–, –(CH₂)₃–, –(CH₂)₄–, –(CH₂)₅–, –(CH₂)₆–, –(CH₂)₇–, –(CH₂)₈–, –CH₂C*HCH₃, and –(CH₂)₄C*(H)(CH₃), in which “C*” denotes a carbon atom from which a hydrogen atom is removed to form a secondary or tertiary alkyl radical. Examples of substituted (C₁–C₅₀)alkylene are substituted (C₁–C₂₀)alkylene, –CF₂–, –C(O)–, and –(CH₂)₁₄C(CH₃)₂(CH₂)₅– (i.e., a 6,6-dimethyl substituted normal-1,20-eicosylene). Since as mentioned previously two R^S may be taken together to form a (C₁–C₁₈)alkylene, examples of substituted (C₁–C₅₀)alkylene also include 1,2-bis(methylene)cyclopentane, 1,2-bis(methylene)cyclohexane, 2,3-bis(methylene)-7,7-dimethyl-bicyclo[2.2.1]heptane, and 2,3-bis(methylene)bicyclo [2.2.2] octane.

[0045] The term “(C₃–C₄₀)cycloalkylene” means a cyclic diradical (i.e., the radicals are on ring atoms) of from 3 to 40 carbon atoms that is unsubstituted or substituted by one or more R^S.

[0046] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of heteroatoms include O, S, S(O), S(O)₂, Si(R^C)₂, P(R^P), N(R^N), –N=C(R^C)₂, –Ge(R^C)₂–, or –Si(R^C)–, where each R^C, each R^N, and each R^P is unsubstituted (C₁–C₁₈)hydrocarbyl or –H. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms are replaced with a heteroatom. The term “(C₁–C₄₀)heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 40 carbon atoms and the term “(C₁–C₄₀)heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 40 carbon atoms, and each heterohydrocarbon has one or more heteroatoms. The radical of the heterohydrocarbyl is on a carbon atom or a heteroatom, and diradicals of the heterohydrocarbyl may be on: (1) one or two carbon atom, (2) one or two heteroatoms, or (3) a carbon atom and a heteroatom. Each (C₁–C₅₀)heterohydrocarbyl and (C₁–C₅₀)heterohydrocarbylene may be unsubstituted or substituted (by

one or more R^S), aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic), or acyclic.

[0047] The (C₁–C₄₀)heterohydrocarbyl may be unsubstituted or substituted (C₁–C₄₀)heteroalkyl, (C₁–C₄₀)hydrocarbyl-O–, (C₁–C₄₀)hydrocarbyl-S–, (C₁–C₄₀)hydrocarbyl-S(O)–, (C₁–C₄₀)hydrocarbyl-S(O)₂–, (C₁–C₄₀)hydrocarbyl-Si(R^C)₂–, (C₁–C₄₀)hydrocarbyl-N(R^N)–, (C₁–C₄₀)hydrocarbyl-P(R^P)–, (C₂–C₄₀)heterocycloalkyl, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)alkylene, (C₃–C₂₀)cycloalkyl-(C₁–C₁₉)heteroalkylene, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)heteroalkylene, (C₁–C₄₀)heteroaryl, (C₁–C₁₉)heteroaryl-(C₁–C₂₀)alkylene, (C₆–C₂₀)aryl-(C₁–C₁₉)heteroalkylene, or (C₁–C₁₉)heteroaryl-(C₁–C₂₀)heteroalkylene.

[0048] The term “(C₄–C₄₀)heteroaryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic heteroaromatic hydrocarbon radical of from 4 to 40 total carbon atoms and from 1 to 10 heteroatoms, and the mono-, bi- or tricyclic radical comprises 1, 2 or 3 rings, respectively, wherein the 2 or 3 rings independently are fused or non-fused and at least one of the 2 or 3 rings is heteroaromatic. Other heteroaryl groups (e.g., (C_x–C_y)heteroaryl generally, such as (C₄–C₁₂)heteroaryl) are defined in an analogous manner as having from x to y carbon atoms (such as 4 to 12 carbon atoms) and being unsubstituted or substituted by one or more than one R^S. The monocyclic heteroaromatic hydrocarbon radical is a 5-membered or 6-membered ring. The 5-membered ring has 5 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1, 2, or 3; and each heteroatom may be O, S, N, or P. Examples of 5-membered ring heteroaromatic hydrocarbon radical are pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; and tetrazol-5-yl. The 6-membered ring has 6 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1 or 2 and the heteroatoms may be N or P. Examples of 6-membered ring heteroaromatic hydrocarbon radical are pyridine-2-yl; pyrimidin-2-yl; and pyrazin-2-yl. The bicyclic heteroaromatic hydrocarbon radical can be a fused 5,6- or 6,6-ring system. Examples of the fused 5,6-ring system bicyclic heteroaromatic hydrocarbon radical are indol-1-yl; and benzimidazole-1-yl. Examples of the fused 6,6-ring system bicyclic heteroaromatic hydrocarbon radical are quinolin-2-yl; and isoquinolin-1-yl. The tricyclic heteroaromatic hydrocarbon radical can be a fused 5,6,5-; 5,6,6-; 6,5,6-; or 6,6,6-ring system. An example of the fused 5,6,5-ring system is 1,7-dihydropyrrolo[3,2-f]indol-1-yl. An example of the fused 5,6,6-ring system is 1H-benzo[f]indol-1-yl. An example of the fused 6,5,6-

ring system is 9H-carbazol-9-yl. An example of the fused 6,5,6- ring system is 9H-carbazol-9-yl. An example of the fused 6,6,6-ring system is acrydin-9-yl.

[0049] The aforementioned heteroalkyl may be saturated straight or branched chain radicals containing (C₁–C₅₀) carbon atoms, or fewer carbon atoms and one or more of the heteroatoms. Likewise, the heteroalkylene may be saturated straight or branched chain diradicals containing from 1 to 50 carbon atoms and one or more than one heteroatoms. The heteroatoms, as defined above, may include Si(R^C)₃, Ge(R^C)₃, Si(R^C)₂, Ge(R^C)₂, P(R^P)₂, P(R^P), N(R^N)₂, N(R^N), N, O, OR^C, S, SR^C, S(O), and S(O)₂, wherein each of the heteroalkyl and heteroalkylene groups are unsubstituted or substituted by one or more R^S.

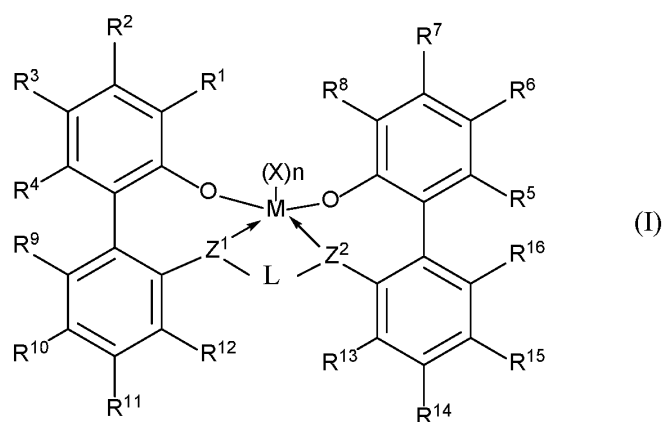
[0050] Examples of unsubstituted (C₂–C₄₀)heterocycloalkyl are unsubstituted (C₂–C₂₀)heterocycloalkyl, unsubstituted (C₂–C₁₀)heterocycloalkyl, aziridin-1-yl, oxetan-2-yl, tetrahydrofuran-3-yl, pyrrolidin-1-yl, tetrahydrothiophen-S,S-dioxide-2-yl, morpholin-4-yl, 1,4-dioxan-2-yl, hexahydroazepin-4-yl, 3-oxa-cyclooctyl, 5-thio-cyclononyl, and 2-aza-cyclodecyl.

[0051] The term “halogen atom” or “halogen” means the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means anionic form of the halogen atom: fluoride (F⁻), chloride (Cl⁻), bromide (Br⁻), or iodide (I⁻).

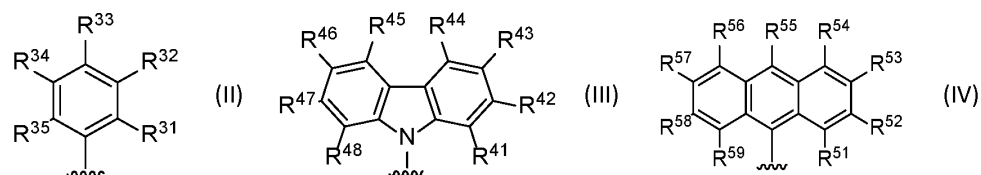
[0052] The term “saturated” means lacking carbon-carbon double bonds, carbon-carbon triple bonds, and (in heteroatom-containing groups) carbon-nitrogen, carbon-phosphorous, and carbon-silicon double bonds. Where a saturated chemical group is substituted by one or more substituents R^S, one or more double and/or triple bonds optionally may or may not be present in substituents R^S. The term “unsaturated” means containing one or more carbon-carbon double bonds, carbon-carbon triple bonds, and (in heteroatom-containing groups) carbon-nitrogen, carbon-phosphorous, and carbon-silicon double bonds, not including any such double bonds that may be present in substituents R^S, if any, or in (hetero) aromatic rings, if any.

[0053] According to some embodiments, the first catalyst system, the second catalyst system, or the third catalyst system may include a metal–ligand complex according to formula (I):

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[0054] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium, the metal being in a formal oxidation state of +2, +3, or +4; n is 0, 1, or 2; when n is 1, X is a monodentate ligand or a bidentate ligand; when n is 2, each X is a monodentate ligand and is the same or different; the metal–ligand complex is overall charge-neutral; each Z is independently chosen from $-O-$, $-S-$, $-N(R^N)-$, or $-P(R^P)-$; L is (C_1-C_{40}) hydrocarbylene or (C_1-C_{40}) heterohydrocarbylene, wherein the (C_1-C_{40}) hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone linking the two Z groups in Formula (I) (to which L is bonded) or the (C_1-C_{40}) heterohydrocarbylene has a portion that comprises a 1-atom to 10-atom linker backbone linking the two Z groups in Formula (I), wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone of the (C_1-C_{40}) heterohydrocarbylene independently is a carbon atom or heteroatom, wherein each heteroatom independently is O, S, S(O), S(O)₂, Si(R^C)₂, Ge(R^C)₂, P(R^C), or N(R^C), wherein independently each R^C is (C_1-C_{30}) hydrocarbyl or (C_1-C_{30}) heterohydrocarbyl; R¹ and R⁸ are independently selected from the group consisting of $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^N)_2NC(O)-$, halogen, and radicals having formula (II), formula (III), or formula (IV):

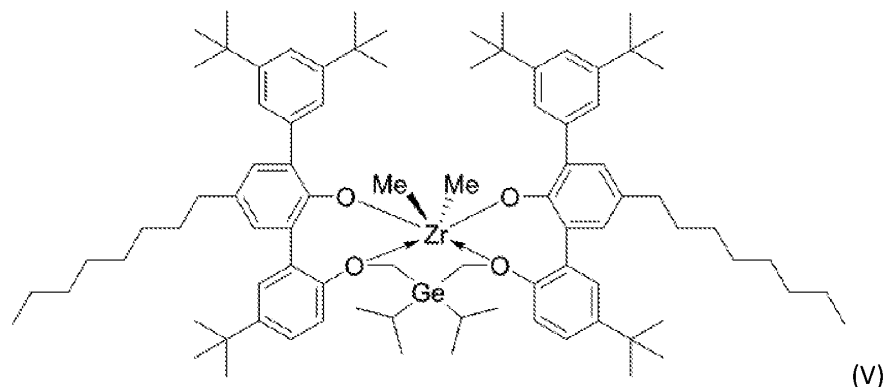


[0055] In formulas (II), (III), and (IV), each of R³¹⁻³⁵, R⁴¹⁻⁴⁸, or R⁵¹⁻⁵⁹ is independently chosen from (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -N=CHR^C, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^N)₂NC(O)-, halogen, or -H, provided at least one of R¹ or R⁸ is a radical having formula (II), formula (III), or formula (IV).

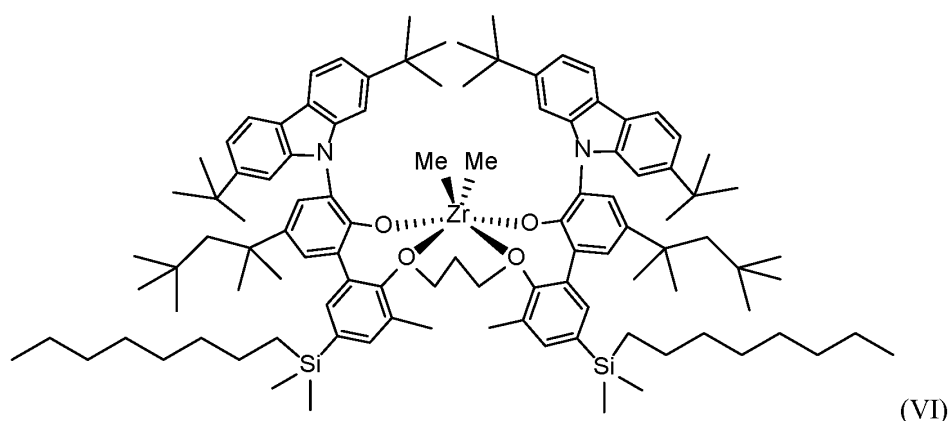
[0056] In formula (I), each of R²⁻⁴, R⁵⁻⁷, and R⁹⁻¹⁶ is independently selected from (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -N=CHR^C, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, halogen, and -H.

[0057] In some embodiments, the multimodal ethylene-based copolymer composition is formed using a first catalyst according to formula (I) in a first reactor and a different catalyst according to formula (I) in a second reactor.

[0058] In one exemplary embodiment where a dual loop reactor is used, the procatalyst used in the first loop is zirconium, [[2,2''-[bis[1-methylethyl]germylene]bis(methyleneoxy-κO)]bis[3'',5,5''-tris(1,1-dimethylethyl)-5'-octyl[1,1':3',1''-terphenyl]-2'-olato-κO]](2-dimethyl-, having the chemical formula C₈₆H₁₂₈F₂GeO₄Zr and the following structure (V):



[0059] In such an embodiment, the procatalyst used in the second loop is zirconium, [[2,2'''-[1,3-propanediylbis(oxy- κ O)]bis[3-[2,7-bis(1,1-dimethylethyl)-9H-carbazol-9-yl]]-5'-(dimethyloctylsilyl)-3'-methyl-5-(1,1,3,3-tetramethylbutyl)[1,1]-biphenyl]-2-olato- κ O]](2-dimethyl, having the chemical formula $C_{107}H_{154}N_2O_4Si_2Zr$ and the following structure (VI):



[0060] According to some embodiments, the first catalyst system, the second catalyst system, or the third catalyst system may include a metal-ligand complex having a constrained geometry structure according to formula (XI):

[0061] $Lp_iMX_mX'_nX''_p$, or a dimer thereof (XI).

[0062] In formula (XI), Lp is an anionic, delocalized, π -bonded group that is bound to M, containing up to 50 non-hydrogen atoms. In some embodiments of formula (XI), two Lp groups may be joined together forming a bridged structure, and further optionally one Lp may be bound to X.

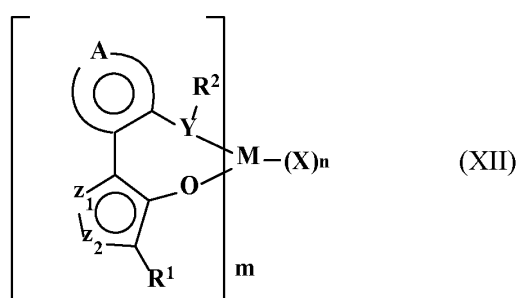
[0063] In formula (XI), M is a metal of Group 4 of the Periodic Table of the Elements in the +2, +3 or +4 formal oxidation state. X is an optional, divalent substituent of up to 50 non-hydrogen atoms that together With Lp forms a metallocycle with M. X' is an optional neutral ligand having up to 20 non hydrogen atoms; each X'' is independently a monovalent, anionic moiety having up to 40 non-hydrogen atoms. Optionally, two X'' groups may be covalently bound together forming a divalent dianionic moiety having both valences bound to M, or, optionally two X'' groups may be covalently bound together to form a neutral, conjugated or nonconjugated diene that is π -

bonded to M, in which M is in the +2 oxidation state. In other embodiments, one or more X'' and one or more X' groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto by means of Lewis base functionality.

[0064] Illustrative Group IV complexes having a constrained geometry structure that may be employed in the practice of the present invention include, but are not limited to:

cyclopentadienyltitaniumtrimethyl; cyclopentadienyltitaniumtriethyl;
cyclopentadienyltitaniumtriisopropyl; cyclopentadienyltitaniumtriphenyl;
cyclopentadienyltitaniumtribenzyl; cyclopentadienyltitanium-2,4-dimethylpentadienyl.

[0065] According to some embodiments, the first catalyst system, the second catalyst system, or the third catalyst system may include a metal–ligand complex according to formula (XII):



[0066] In formula (XII), M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4; and each X is a monodentate or bidentate ligand independently chosen from unsaturated (C₂–C₅₀)heterohydrocarbon, unsaturated (C₂–C₅₀)hydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C₄–C₁₂)diene, halogen, –N(R^N)₂, and –NCOR^C. Subscript n of (X)_n is an interger 1, 2, or 3. Subscript m is 1 or 2. The metal–ligand complex of formula (I) has 6 or fewer metal–ligand bonds and may be charge neutral or have a positive charge associated with the metal center. Each Y is independently selected from oxygen or sulfur.

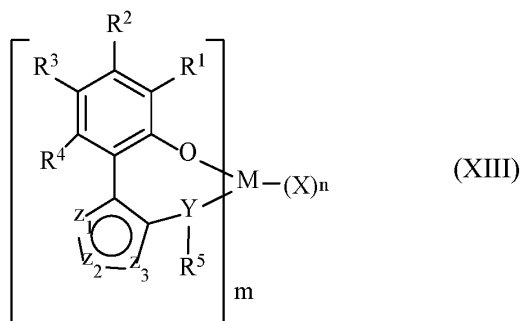
[0067] In formula (XII), each R¹ is independently selected from the group consisting of (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^P)₂P(O)–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, and –H. Each R² is independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl,

(C₄–C₅₀)heteroaryl, –Si(R^C)₃, and –Ge(R^C)₃, and, when m is 2, two R² are optionally covalently linked; and for each individual ring containing groups z₁ and z₂, each of z₁ and z₂ is independently selected from the group consisting of sulfur, oxygen, –N(R^R)–, and –C(R^R)–, provided that at least one of z₁ or z₂ is –C(R^R)–.

[0068] In formula (XII), each A is independently chosen from –z₃–z₄–z₅– or –C(R³)C(R⁴)C(R⁵)C(R⁶)–, such that when A is –z₃–z₄–z₅–, each of z₃, z₄, and z₅ is selected from the group consisting of sulfur, oxygen, –N(R^R)–, and –C(R^R)–, provided that exactly one of z₃, z₄, or z₅ is –C(R^R)– or that exactly two of z₃, z₄, or z₅ are –C(R^R)–. When A is –C(R³)C(R⁴)C(R⁵)C(R⁶)–, each R³, R⁴, R⁵, and R⁶ is independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^P)₂P(O)–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, or –H.

[0069] Each R^C, R^N, and R^P in formula (XII) is independently a (C₁–C₅₀)hydrocarbyl; and each R^R is independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^P)₂P(O)–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, or –H, wherein any two R^R groups bonded to neighboring atoms are optionally linked.

[0070] According to some embodiments, the first catalyst system, the second catalyst system, or the third catalyst system may include a metal–ligand complex according to formula (XIII):



[0071] In formula (XIII), M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4. Each X is a monodentate or bidentate ligand independently chosen from (C₁–C₅₀)hydrocarbon, (C₁–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C₄–C₁₂)diene, halogen, –N(R^N)₂, and –NCOR^C. Subscript n is 1, 2 or 3. Subscript m is 1 or 2. The metal–ligand complex of formula (XIII) has 6 or fewer metal–ligand bonds and is overall charge-neutral.

[0072] In embodiments of formula (XIII), each Y is independently selected from oxygen or sulfur. Each R¹, R², R³, and R⁴ is independently selected from the group consisting of (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, and –H. Each R⁵ is independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, and –Ge(R^C)₃, and, when m is 2, two R⁵ are optionally covalently linked.

[0073] In embodiments of formula (XIII), for each individual ring containing groups z₁, z₂, and z₃, each of z₁, z₂, and z₃ is independently selected from the group consisting of sulfur, oxygen, –N(R^R)–, or –C(R^R)– and at least one and not more than two of z₁, z₂, and z₃ are –C(R^R)–, where R^R is –H or (C₁–C₃₀)hydrocarbyl, wherein any two R^R groups bonded to neighboring atoms are optionally linked. In formula (XIII), each R^C, R^N, and R^P in formula (XIII) is independently a (C₁–C₃₀)hydrocarbyl.

[0074] In the catalyst systems according to embodiments of this disclosure, the molar ratio of the bimetallic activator complex to Group IV metal–ligand complex may be from 1:10,000 to 1000:1, such as, for example, from 1:5000 to 100:1, from 1:100 to 100:1 from 1:10 to 10:1, from 1:5 to 1:1, or from 1.25:1 to 1:1. The catalyst systems may include combinations of one or more bimetallic activator complex described in this disclosure.

[0075] Co-Catalyst Component

[0076] The catalyst system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts

of olefin polymerization reactions. For example, the system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Suitable activating co-catalysts for use herein include alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0077] Lewis acid activators (co-catalysts) include Group 13 metal compounds containing from 1 to 3 (C₁–C₂₀)hydrocarbyl substituents as described herein. In one embodiment, Group 13 metal compounds are tri((C₁–C₂₀)hydrocarbyl)-substituted-aluminum or tri((C₁–C₂₀)hydrocarbyl)-boron compounds. In embodiments, Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum, tri((C₁–C₂₀)hydrocarbyl)-boron compounds, tri((C₁–C₁₀)alkyl)aluminum, tri((C₆–C₁₈)aryl)boron compounds, and halogenated (including perhalogenated) derivatives thereof. In further embodiments, Group 13 metal compounds are tris(fluoro-substituted phenyl)boranes, tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tris((C₁–C₂₀)hydrocarbyl borate (e.g. trityl tetrafluoroborate) or a tri((C₁–C₂₀)hydrocarbyl)ammonium tetra((C₁–C₂₀)hydrocarbyl)borane (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁–C₂₀)hydrocarbyl)₄N⁺, a ((C₁–C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁–C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁–C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁–C₂₀)hydrocarbyl, when two or more are present, may be the same or different.

[0078] Combinations of neutral Lewis acid activators (co-catalysts) include mixtures comprising a combination of a tri((C₁–C₄)alkyl)aluminum and a halogenated tri((C₆–C₁₈)aryl)boron compound, especially a tris(pentafluorophenyl)borane. Embodiments are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a

polymeric or oligomeric alumoxane. Ratios of numbers of moles of (metal–ligand complex): (tris(pentafluoro-phenylborane): (alumoxane) [e.g., (Group 4 metal–ligand complex) : (tris(pentafluoro-phenylborane): (alumoxane))] are from 1:1:1 to 1:10:30, in embodiments, from 1:1:1.5 to 1:5:10

[0079] The catalyst system comprising the metal–ligand complex of formula (I) may be activated to form an active catalyst composition by combination with one or more co-catalysts, for example, a cation forming co-catalyst, a strong Lewis acid, or combinations thereof. Suitable activating co-catalysts include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to: modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1[−]) amine, and combinations thereof.

[0080] In some embodiments, one or more of the foregoing activating co-catalysts are used in combination with each other. An especially preferred combination is a mixture of a tri((C₁–C₄)hydrocarbyl)aluminum, tri((C₁–C₄)hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound. The ratio of total number of moles of one or more metal–ligand complexes of formula (I) to total number of moles of one or more of the activating co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some embodiments, at least 1:1000; and 10:1 or less, and in some embodiments, 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, preferably the number of moles of the alumoxane that are employed is at least 100 times the number of moles of the metal–ligand complex of formula (I). When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, in some embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal–ligand complexes of formula (I) from 0.5: 1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal–ligand complexes of formula (I).

[0081] Compositions

[0082] It was discovered that by performing processes as described above, multimodal ethylene-based copolymer compositions with improved melt strength can be produced. Properties

of the multimodal ethylene-based copolymer composition according to embodiments disclosed and described herein will now be provided. It should be understood that by modifying the various process conditions described above embodiments of the multimodal ethylene-based copolymer composition with differing and desirable properties can be produced. Although the properties listed below are recited in separate paragraphs, it should be understood that any property from any paragraph below may be combined with any other property from any paragraph below by modifying the various process conditions discussed above. Therefore, the multimodal ethylene-based copolymer composition having any combination of various properties listed below are envisioned and can be produced, according to embodiments.

[0083] In one or more embodiments, the multimodal ethylene-based copolymer composition may have a density of 0.900 g/cm³ to 0.930 g/cm³. For example, embodiments of the presently-disclosed multimodal ethylene-based copolymer composition may have densities of from 0.900 g/cm³ to 0.925 g/cm³, from 0.900 g/cm³ to 0.920 g/cm³, from 0.900 g/cm³ to 0.918 g/cm³, from 0.900 g/cm³ to 0.916 g/cm³, from 0.900 g/cm³ to 0.914 g/cm³, from 0.900 g/cm³ to 0.912 g/cm³, from 0.900 g/cm³ to 0.910 g/cm³, from 0.900 g/cm³ to 0.908 g/cm³, from 0.900 g/cm³ to 0.906 g/cm³, from 0.900 g/cm³ to 0.904 g/cm³, from 0.900 g/cm³ to 0.902 g/cm³, from 0.902 g/cm³ to 0.920 g/cm³, from 0.902 g/cm³ to 0.918 g/cm³, from 0.902 g/cm³ to 0.916 g/cm³, from 0.902 g/cm³ to 0.914 g/cm³, from 0.902 g/cm³ to 0.912 g/cm³, from 0.902 g/cm³ to 0.910 g/cm³, from 0.902 g/cm³ to 0.908 g/cm³, from 0.902 g/cm³ to 0.906 g/cm³, from 0.902 g/cm³ to 0.904 g/cm³, from 0.904 g/cm³ to 0.920 g/cm³, from 0.904 g/cm³ to 0.918 g/cm³, from 0.904 g/cm³ to 0.916 g/cm³, from 0.904 g/cm³ to 0.914 g/cm³, from 0.904 g/cm³ to 0.912 g/cm³, from 0.904 g/cm³ to 0.910 g/cm³, from 0.904 g/cm³ to 0.908 g/cm³, from 0.904 g/cm³ to 0.906 g/cm³, from 0.906 g/cm³ to 0.920 g/cm³, from 0.906 g/cm³ to 0.918 g/cm³, from 0.906 g/cm³ to 0.916 g/cm³, from 0.906 g/cm³ to 0.914 g/cm³, from 0.906 g/cm³ to 0.912 g/cm³, from 0.906 g/cm³ to 0.910 g/cm³, from 0.906 g/cm³ to 0.908 g/cm³, from 0.908 g/cm³ to 0.920 g/cm³, from 0.908 g/cm³ to 0.918 g/cm³, from 0.908 g/cm³ to 0.916 g/cm³, from 0.908 g/cm³ to 0.914 g/cm³, from 0.908 g/cm³ to 0.912 g/cm³, from 0.908 g/cm³ to 0.910 g/cm³, from 0.910 g/cm³ to 0.920 g/cm³, from 0.910 g/cm³ to 0.918 g/cm³, from 0.910 g/cm³ to 0.916 g/cm³, from 0.910 g/cm³ to 0.914 g/cm³, from 0.910 g/cm³ to 0.912 g/cm³, from 0.912 g/cm³ to 0.920 g/cm³, from 0.912 g/cm³ to 0.918 g/cm³, from 0.912 g/cm³ to 0.916 g/cm³, from 0.912 g/cm³ to 0.914 g/cm³, from 0.914 g/cm³ to 0.920 g/cm³, from 0.914 g/cm³ to 0.918 g/cm³, from 0.914 g/cm³ to 0.916 g/cm³, from 0.916 g/cm³ to 0.920 g/cm³, from 0.916 g/cm³ to 0.918 g/cm³, from 0.918 g/cm³ to 0.920 g/cm³, or any combination of these ranges.

[0084] In one or more embodiments, the multimodal ethylene-based copolymer composition may have a melt index (I_2) of from 0.50 g/10 minutes (g/10 min) to 10.0 g/10 min when measured according to ASTM D-1238 at 190 °C and 2.16 kg. In one or more embodiments, the multimodal ethylene-based copolymer composition may have a melt index (I_2) of from 0.5 g/10 min to 10.0 g/10 min, from 0.5 g/10 min to 9.0 g/10 min, from 0.5 g/10 min to 8.0 g/10 min, from 0.5 g/10 min to 7.0 g/10 min, from 0.5 g/10 min to 6.0 g/10 min, from 0.5 g/10 min to 5.0 g/10 min, from 0.5 g/10 min to 4.0 g/10 min, from 0.5 g/10 min to 3.0 g/10 min, from 0.5 g/10 min to 2.0 g/10 min, from 0.5 g/10 min to 1.0 g/10 min, from 1.0 g/10 min to 10.0 g/10 min, from 1.0 g/10 min to 9.0 g/10 min, from 1.0 g/10 min to 8.0 g/10 min, from 1.0 g/10 min to 7.0 g/10 min, from 1.0 g/10 min to 6.0 g/10 min, from 1.0 g/10 min to 5.0 g/10 min, from 1.0 g/10 min to 4.0 g/10 min, from 1.0 g/10 min to 3.0 g/10 min, from 1.0 g/10 min to 2.0 g/10 min, from 2.0 g/10 min to 10.0 g/10 min, from 2.0 g/10 min to 9.0 g/10 min, from 2.0 g/10 min to 8.0 g/10 min, from 2.0 g/10 min to 7.0 g/10 min, from 2.0 g/10 min to 6.0 g/10 min, from 2.0 g/10 min to 5.0 g/10 min, from 2.0 g/10 min to 4.0 g/10 min, from 2.0 g/10 min to 3.0 g/10 min, from 3.0 g/10 min to 10.0 g/10 min, from 3.0 g/10 min to 9.0 g/10 min, from 3.0 g/10 min to 8.0 g/10 min, from 3.0 g/10 min to 7.0 g/10 min, from 3.0 g/10 min to 6.0 g/10 min, from 3.0 g/10 min to 5.0 g/10 min, from 3.0 g/10 min to 4.0 g/10 min, from 4.0 g/10 min to 10.0 g/10 min, from 4.0 g/10 min to 9.0 g/10 min, from 4.0 g/10 min to 8.0 g/10 min, from 4.0 g/10 min to 7.0 g/10 min, from 4.0 g/10 min to 6.0 g/10 min, from 4.0 g/10 min to 5.0 g/10 min, from 5.0 g/10 min to 10.0 g/10 min, from 5.0 g/10 min to 9.0 g/10 min, from 5.0 g/10 min to 8.0 g/10 min, from 5.0 g/10 min to 7.0 g/10 min, from 5.0 g/10 min to 6.0 g/10 min, from 6.0 g/10 min to 10.0 g/10 min, from 6.0 g/10 min to 9.0 g/10 min, from 6.0 g/10 min to 8.0 g/10 min, from 6.0 g/10 min to 7.0 g/10 min, from 7.0 g/10 min to 10.0 g/10 min, from 7.0 g/10 min to 9.0 g/10 min, from 7.0 g/10 min to 8.0 g/10 min, from 8.0 g/10 min to 10.0 g/10 min, from 8.0 g/10 min to 9.0 g/10 min, from 9.0 g/10 min to 10.0 g/10 min, or any combination of these ranges, when measured according to ASTM D-1238 at 190 °C and 2.16 kg.

[0085] According to embodiments, the multimodal ethylene-based copolymer composition may have a molecular weight distribution, expressed as the ratio of the weight average molecular weight to number average molecular weight (M_w/M_n), in the range of from 2.0 to 6.0. For example, the multimodal ethylene-based copolymer composition may have a molecular weight distribution of from 2.0 to 5.5, 2.0 to 5.0, 2.0 to 4.5, 2.0 to 4.0, 2.0 to 3.5, 2.0 to 3.0, 2.0 to 2.5, 2.5 to 6.0, 3.0 to 5.5, 3.0 to 5.0, 3.0 to 4.5, 3.0 to 4.0, 3.0 to 3.5, 3.5 to 6.0, 3.5 to 5.5, 3.5 to 5.0, 3.5 to 4.5, 3.5 to 4.0, 4.0 to 6.0, 4.0 to 5.5, 4.0 to 5.0, 4.0 to 4.5, 4.5 to 6.0, 4.5 to 5.5, 4.5 to 5.0,

5.0 to 6.0, 5.0 to 5.5, or 5.5 to 6.0, or any combination of these ranges. As presently described, the molecular weight distribution may be calculated according to gel permeation chromatography (GPC) techniques as described herein.

[0086] The long chain branching frequency (LCB_f) refers to the level of long chain branches per 1000 carbons. In embodiments, the long chain branching frequency (LCB_f) of the multimodal ethylene-based copolymer composition is greater than or equal to 1.0 and less than or equal to 1.8. In one or more embodiments, the long chain branching frequency (LCB_f) of the multimodal ethylene-based copolymer composition may be from 1.0 to 1.8, from 1.0 to 1.6, from 1.0 to 1.4, from 1.0 to 1.2, from 1.2 to 1.8, from 1.2 to 1.6, from 1.2 to 1.4, from 1.4 to 1.8, from 1.4 to 1.6, from 1.6 to 1.8, or any combination of these ranges.

[0087] According to embodiments, the multimodal ethylene-based copolymer composition may have an activation energy (E_a) of the composition as determined from dynamic mechanical analysis may be greater than 30 kJ/mol. In further embodiments, the multimodal ethylene-based copolymer compositions may have an activation energy (E_a) of the composition as determined from dynamic mechanical analysis may be from 30 kJ/mol to 60 kJ/mol, from 30 kJ/mol to 50 kJ/mol, from 30 kJ/mol to 40 kJ/mol, from 40 kJ/mol to 60 kJ/mol, from 40 kJ/mol to 50 kJ/mol, or from 50 kJ/mol to 60 kJ/mol.

[0088] The activation energy is calculated from rheology time-temperature superposition viscosity data obtained from melt rheology frequency sweeps. These measurements are performed using TA Instruments Advanced Rheometric Expansion System (ARES) equipped with 25 mm parallel plates using nitrogen pure. The linear viscoelastic response are measured at three different temperatures 150 °C, 190 °C, and 230 °C, using frequencies of 0.1 – 500 rad/s., 0.1 – 100 rad/s, and 0.01 – 100 rad/s, respectively. The strain is altered based on transducer torque output, making sure torque remained with acceptable range. The stress response is analyzed in terms of amplitude and phase, from which the storage and loss moduli and dynamic melt viscosity are calculated. The temperature dependence of linear viscoelastic curve can be predicted by shifting the modulus curves across the frequency axis (X-axis) against a reference using sets of shift factors. This concept is generally known as time-temperature superposition. This technique involves shifting curves at different temperatures in such a way that they overlap and form a single curve, also known as the master curve. The shift factors were generated using RepTate software. Reference

temperature was chosen at 190 °C. The Arrhenius equation associates the horizontal shift factors to the activation energy and a reference temperature according to the following equation:

$$a_T = e^{\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} \quad (\text{EQ. 1})$$

[0089] According to embodiments, the multimodal ethylene-based copolymer composition may have a melt strength (MS) that satisfies the following equation 1:

$$MS = \frac{x}{I_2} + y \quad (\text{EQ. 2})$$

[0090] wherein x is greater than or equal to 8, y is greater than or equal to 3, and I_2 is a melt index of the copolymer measured according to ASTM 1238 at 2.16 kg and 190 °C. According to one or more embodiments, the multimodal ethylene-based copolymer composition may have a melt strength of at least 5 centiNewtons (cN). In further embodiments, the multimodal ethylene-based copolymer composition may have a melt strength of from 5 cN to 50 cN, from 5 cN to 45 cN, from 5 cN to 40 cN, from 5 cN to 35 cN, from 5 cN to 30 cN, from 5 cN to 25 cN, from 5 cN to 20 cN, from 5 cN to 15 cN, from 5 cN to 10 cN, from 10 cN to 50 cN, from 10 cN to 45 cN, from 10 cN to 40 cN, from 10 cN to 35 cN, from 10 cN to 30 cN, from 10 cN to 25 cN, from 10 cN to 20 cN, from 10 cN to 15 cN, from 15 cN to 50 cN, from 15 cN to 45 cN, from 15 cN to 40 cN, from 15 cN to 35 cN, from 15 cN to 30 cN, from 15 cN to 25 cN, from 15 cN to 20 cN, from 20 cN to 50 cN, from 20 cN to 45 cN, from 20 cN to 40 cN, from 20 cN to 35 cN, from 20 cN to 30 cN, from 20 cN to 25 cN, from 25 cN to 50 cN, from 25 cN to 45 cN, from 25 cN to 40 cN, from 25 cN to 35 cN, from 25 cN to 30 cN, from 30 cN to 50 cN, from 30 cN to 45 cN, from 30 cN to 40 cN, from 30 cN to 35 cN, from 35 cN to 50 cN, from 35 cN to 45 cN, from 35 cN to 40 cN, from 40 cN to 50 cN, from 40 cN to 45 cN, or from 45 cN to 50 cN.

[0091] In embodiments, the multimodal ethylene-based copolymer composition may have a ratio of viscosity measured at 0.1 radians/second and 190 °C to viscosity measured at 100 radians/second and 190 °C ($V_{0.1}/V_{100}$), as determined by dynamic mechanical analysis, of greater than 5. In further embodiments, the multimodal ethylene-based copolymer composition may have a ($V_{0.1}/V_{100}$), as determined by dynamic mechanical analysis, of from 5 to 30, from 5 to 25, from 5 to 20, from 5 to 15, from 5 to 10, from 10 to 30, from 10 to 25, from 10 to 20, from 10 to 15, from 15 to 30, from 15 to 25, from 15 to 20, from 20 to 30, from 20 to 25, or from 25 to 30.

[0092] In embodiments, the cumulative distribution fractions (CDF) for light scattering analysis (CDF_{LS}) at a molecular weight greater than 500,000 g/mol is greater than or equal to 8%.

[0093] In embodiments, the multimodal ethylene-based copolymer composition may have a high molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using GPC molecular weight distribution, of from 8% to 50%. In embodiments, the high molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using GPC molecular weight distribution, may be from 8% to 40%, from 8% to 30%, from 8% to 20%, from 8% to 10%, from 10% to 50%, from 10% to 40%, from 10% to 30%, from 10% to 20%, from 20% to 50%, from 20% to 40%, from 20% to 30%, from 30% to 50%, from 30% to 40%, or from 40% to 50%.

[0094] In embodiments, the multimodal ethylene-based copolymer composition may have a low molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram less than 500,000 g/mol using GPC molecular weight distribution, of greater than 50%. In embodiments, the low molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram less than 500,000 g/mol using GPC molecular weight distribution, may be from 50% to 92%, from 50% to 90%, from 50% to 80%, from 50% to 70%, from 50% to 60%, from 60% to 92%, from 60% to 90%, from 60% to 80%, from 60% to 70%, from 70% to 92%, from 70% to 90%, from 70% to 80%, from 80% to 92%, from 80% to 90%, or from 90% to 92%. Traditionally, it was thought that having as much high molecular weight material as possible was ideal because high molecular weight would lead to higher levels of entanglements that improve the properties of the LLDPE. Accordingly, low molecular weight material was kept to a minimum. However, the multimodal ethylene-based copolymer compositions according to embodiments disclosed and described herein exhibit unique and unexpected characteristics compared to commercially available LDPE products when the high molecular weight fraction, computed by measuring an area fraction of a low angle light scattering (LALLS) detector chromatogram greater than 500,000 g/mol using GPC molecular weight distribution, is from 8% to 50%.

[0095] In embodiments, the amount of long-chain branching derived from the concentration of vinyl end groups in the multimodal ethylene-based copolymer composition produced expressed in the vinyl groups/1,000 carbon atoms may be from 0.475 to 0.600. In embodiments, the amount

of long-chain branching derived from the concentration of vinyl groups in the multimodal ethylene-based copolymer composition produced expressed in vinyls/1,000 carbon atoms may be from 0.475 to 0.575, from 0.475 to 0.550, from 0.475 to 0.525, from 0.475 to 0.500, from 0.500 to 0.600, from 0.500 to 0.575, from 0.500 to 0.550, from 0.500 to 0.525, from 0.525 to 0.600, from 0.525 to 0.575, from 0.525 to 0.550, from 0.550 to 0.600, from 0.550 to 0.575, or from 0.575 to 0.600. Without intent to be bound by theory, it is believed that the vinyl end groups enable the formation of long chain branching, which is a contributing factor to the melt strengths achieved.

[0096] The multimodal ethylene-based copolymer compositions may further comprise one or more additives. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers, and combinations thereof. The multimodal ethylene-based copolymer compositions may contain any amounts of additives. The multimodal ethylene-based copolymer compositions may comprise from about 0 to about 10 percent by the combined weight of such additives, based on the total weight of the multimodal ethylene-based copolymer compositions. The multimodal ethylene-based copolymer compositions may further comprise fillers, which may include, but are not limited to, organic or inorganic fillers. The multimodal ethylene-based copolymer compositions may contain from about 0 to about 20 weight percent fillers such as, for example, calcium carbonate, talc, or $\text{Mg}(\text{OH})_2$, based on the total weight of the multimodal ethylene-based copolymer compositions. The multimodal ethylene-based copolymer compositions may further be blended with one or more polymers to form a blend.

[0097] TEST METHODS

[0098] Unless otherwise indicated herein, the following analytical methods are used in describing aspects of the present disclosure:

[0099] Melt index

[00100] Melt indices I_2 (or I_2) and I_{10} (or I_{10}) of polymer samples were measured in accordance to ASTM D-1238 (method B) at 190 °C and at 2.16 kg and 10 kg load, respectively. Their values are reported in g/10 min.

[00101] Density

[00102] Samples for density measurement were prepared according to ASTM D4703. Measurements were made, according to ASTM D792, Method B, within one hour of sample pressing.

[00103] **Triple Detector Gel Permeation Chromatography (GPC)**

[00104] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the column and detector compartment were set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00105] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

[00106] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under “low speed” shaking.

[00107] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated

as Equation 1. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/- 0.5% of the nominal flowrate.

[00108] For the determination of the viscometer and light scattering detector offsets from the IR5 detector, the Systematic Approach for the determination of multi-detector offsets is done in a manner consistent with that published by Balke, Mourey, et. al. (Mourey and Balke, Chromatography Polym. Chpt 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, Chromatography Polym. Chpt 13, (1992)), optimizing triple detector log (MW and IV) results from a linear homopolymer polyethylene standard ($3.5 > M_w/M_n > 2.2$) with a molecular weight in the range of 115,000 to 125,000 g/mol to the narrow standard column calibration results from the narrow standards calibration curve using PolymerChar GPCOne™ Software.

[00109] The absolute molecular weight data was obtained in a manner consistent with that published by Zimm (Zimm, B.H., J. Chem. Phys., 16, 1099 (1948)) and Kratochvil (Kratochvil, P., Classical Light Scattering from Polymer Solutions, Elsevier, Oxford, NY (1987)) using PolymerChar GPCOne™ software. The overall injected concentration, used in the determination of the molecular weight, was obtained from the mass detector area and the mass detector constant, derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards of known weight-average molecular weight. The calculated molecular weights (using GPCOne™) were obtained using a light scattering constant, derived from one or more of the polyethylene standards mentioned below, and a refractive index concentration coefficient, dn/dc , of -0.104. Generally, the mass detector response (IR5) and the light scattering constant (determined using GPCOne™) should be determined from a linear standard with a molecular weight in excess of about 50,000 g/mole. The viscometer calibration (determined using GPCOne™) can be accomplished using the methods described by the manufacturer, or, alternatively, by using the published values of suitable linear standards, such as Standard Reference Materials (SRM) 1475 (available from National Institute of Standards and Technology (NIST)). A viscometer constant (obtained using GPCOne™) is calculated which relates specific viscosity area (DV) and injected mass for the calibration standard to its intrinsic viscosity. The chromatographic concentrations are assumed low enough to eliminate addressing 2nd virial coefficient effects (concentration effects on molecular weight).

[00110] The absolute weight average molecular weight ($MW_{(Abs)}$) is obtained (using GPCOne™) from the Area of the Light Scattering (LS) integrated chromatogram (factored by the light scattering constant) divided by the mass recovered from the mass constant and the mass detector (IR5) area. The molecular weight and intrinsic viscosity responses are linearly extrapolated at chromatographic ends where signal to noise becomes low (using GPCOne™). Other respective moments, $Mn_{(Abs)}$ and $Mz_{(Abs)}$ are be calculated according to equations 8-10 as follows:

$$Mn_{(Abs)} = \frac{\sum^i IR_i}{\sum^i \left(\frac{IR_i}{M_{Absolute_i}} \right)} \quad (EQ. 3)$$

$$Mw_{(Abs)} = \frac{\sum^i IR_i \times M_{Absolute_i}}{\sum^i IR_i} \quad (EQ. 4)$$

$$Mz_{(Abs)} = \frac{\sum^i \left(IR_i * M_{Absolute_i}^2 \right)}{\sum^i \left(IR_i * M_{Absolute_i} \right)} \quad (EQ. 5)$$

[00111] CDF Calculation Method

[00112] The calculation of the cumulative detector fractions (CDF) for the low angle laser light scattering detector (“CDF_{LS}”) are accomplished by the following steps:

[00113] 1) Linearly flow correct the chromatogram based on decane flow marker injection as described above.

[00114] 2) Perform detector offsets as described above.

[00115] 3) Calculate absolute molecular weights from light scattering as described above.

[00116] 4) Calculate the cumulative detector fraction (CDF) of the Low-Angle Laser Light Scattering (LALLS) chromatogram (CDF_{LS}) based on its baseline-subtracted peak height (H) from high to low molecular weight (low to high retention volume) at each data slice (j) according to Equations 13.

$$CDF_{LS \geq 500,000 MW} = \frac{\sum_{j=RV \text{ at } 500,000 \text{ MW}}^{j=RV \text{ at Highest Integrated Volume}} H_j}{\sum_{j=RV \text{ at Lowest Integrated Volume}}^{j=RV \text{ at Highest Integrated Volume}} H_j} \quad (\text{EQ. 6})$$

[00117] Calculation of LCB frequency (LCBr)

[00118] The long chain branching frequency was calculated based on the differences between the g' , which is a ratio of the intrinsic viscosity of a polymer sample over a linear polymer reference with the same molecular weight. In 3D GPC practice, a reference polyethylene homopolymer, containing no detectable LCB or SCB, and with a Mw of approximately 120,000 g/mol and polydispersity around 3.0, is injected at the beginning of each run queue to establish the Mark-Houwink linear reference line. A first-order linear fit is applied to the obtained log of the intrinsic viscosity and log of the molecular weight data within the log of the molecular weight range of 4.5 to 5.8 g/mol to provide the linear reference K and α values.

[00119] A polyethylene sample of interest is analyzed to obtain intrinsic viscosity, molecular weight values, and the value of g'_i is calculated at each chromatographic slice (i) according to Equation 14:

$$g'_i = (IV_{\text{Sample},i} / IV_{\text{linear reference},i}) \quad (\text{EQ. 7})$$

[00120] where the calculation utilizes the $IV_{\text{Sample},i}$ at equivalent absolute molecular weight values and same SCB content values to the linear reference within the log molecular weight range of 4.5 to 5.8 g/mol. If a difference in SCB content exists, the $IV_{\text{linear reference},i}$ line is vertically shifted by adjusting the K value from the Mark-Houwink Plot to account for the SCB correction compared to the $IV_{\text{Sample},i}$. The shift is done until the linear reference line makes a single point of contact to make a tangent with the sample Mark-Houwink line at a log molecular weight of 4.5.

[00121] A Zimm-Stockmayer branching factor g was calculated from g' , $g' = g^\epsilon$, using an epsilon factor of 0.5. The number of branches along the polymer sample (B_n) at each data slice (i) can be determined by using Equation 15, (B. H. Zimm and W. H. Stockmayer, J. Chem. Phys. **17**, 1301 (1949)):

$$g = \left[\left(1 + \frac{B_{n,i}}{7} \right)^{1/2} + \frac{4}{9} \frac{B_{n,i}}{\pi} \right]^{-1/2} \quad (\text{EQ. 8})$$

[00122] Finally, the average LCBf quantity per 1000 carbons in the polymer across all of the slices (i) can be determined using Equation 16:

$$LCBf = \frac{\sum_i \left(\frac{B_{n,i}}{M_i / 14000} c_i \right)}{\sum_i c_i} \quad (\text{EQ. 9})$$

[00123] Procedure for NMR end group analysis including vinyl count determination

[00124] Approximately 7 mg of polymer sample was loaded into a 5mm NMR tube with 0.6 ml tetrachloroethane- d_2 with 0.008 M chromium(III) acetylacetonate. The tube was purged with N_2 , and the cap was secured with Teflon tape. The prepared sample tube was heated in a heating block set at 125 °C and repeatedly vortexed until a homogeneous solution was achieved evidenced by consistent flow when the tube was tipped horizontally. The finished sample was inserted into a Bruker AVANCE 600 MHz system equipped with a 10 mm high-temperature cryo-probe set at 120 °C. The acquisition parameters for the 1H NMR spectra are: 90 degree pulse, 1.8 second acquisition time, 10 seconds relaxation delay, center of spectrum set at 2 ppm, spectral width of 20 ppm and 128 scans for signal averaging. The resulting raw FID was exponential multiplied, Fourier transformed, phased, baseline corrected, and integrated using MNOVA software.

Semi-Batch Reactor Polymerization Procedure

[00125] Raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked ISOPAR E commercially available from ExxonMobil Corporation) are purified with molecular sieves before introduction into the reaction environment. A one gallon (3.79 L) stirred autoclave reactor was charged with ISOPAR E, and 1-octene. The reactor was then heated to the desired temperature and charged with ethylene to reach the desired pressure. Hydrogen was also added at this point if desired. The catalyst composition was prepared in a drybox under inert atmosphere by mixing the desired pro-catalyst and optionally one or more additives as desired, with additional solvent to give a total volume of about 15-20 mL. The activated catalyst mixture was then quick-injected into the reactor. The reactor pressure and temperature were kept constant by feeding ethylene during the polymerization and cooling the reactor as needed. After 10 minutes, the ethylene feed was shut off and the solution transferred

into a nitrogen-purged resin kettle. The polymer was thoroughly dried in a vacuum oven, and the reactor was thoroughly rinsed with hot ISOPAR E between polymerization runs.

Procedure for Polymerization in a Continuous Reactor

[00126] Raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked Isopar E commercially available from ExxonMobil Corporation) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to above reaction pressure. The solvent and comonomer (1-octene) feed are pressurized via a mechanical positive displacement pump to above reaction pressure. MMAO-3A, commercially available from Nouryon, was used as an impurity scavenger. The individual catalyst components (procatalyst or cocatalyst) were manually batch diluted to specified component concentrations with purified solvent (Isopar E) and pressured to above reaction pressure. The cocatalyst is $[\text{HNMe}(\text{C}_{18}\text{H}_{37})]_2$ $[\text{B}(\text{C}_6\text{F}_5)_4]$, commercially available from Boulder Scientific, and is used at a 1.2 ratio to catalyst metal unless otherwise specified. All reaction feed flows were measured with mass flow meters and independently controlled with computer automated valve control systems.

[00127] The continuous solution polymerizations were carried out in one or more of a CSTR, loop, and/or a plug flow reactor. The CSTR and loop reactors have independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The plug flow reactor has independent control of catalyst component feeds. The combined solvent, monomer, comonomer and hydrogen feed to the reactors is temperature controlled to anywhere between 5 °C to 50 °C and typically 25 °C. The fresh comonomer feed to the polymerization reactor is fed in with the solvent feed. The fresh solvent feed is controlled typically with each injector receiving half of the total fresh feed mass flow. The cocatalyst is fed based on a calculated specified molar ratio to the procatalysts. Immediately following each fresh injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The ratio of the catalyst feeds is adjusted to obtain the desired polymer MI, density, and melt strength. The effluent from the polymerization reactor system (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits and passes through a control valve (responsible for maintaining the pressure of the reactor system at a specified target). As the stream

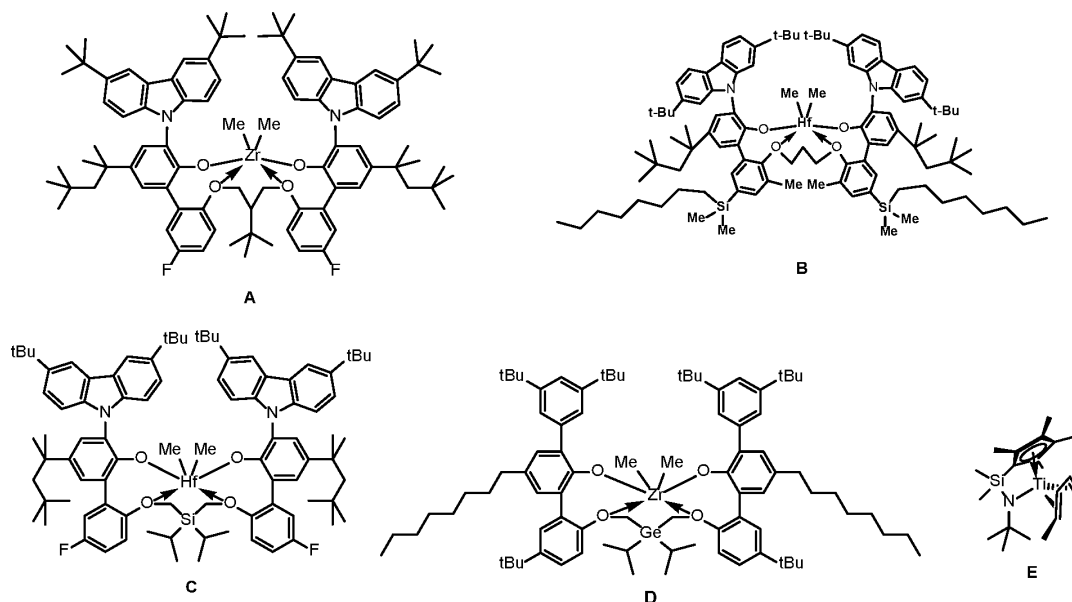
exits the reactor it is contacted with water to stop the reaction. In addition, various additives, such as antioxidants, could be added at this point. The stream then goes through another set of static mixing elements to evenly disperse the catalyst kill and additives.

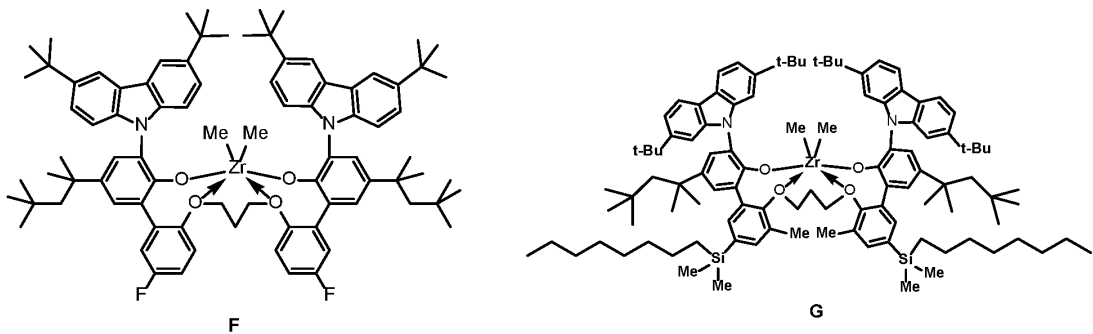
[00128] Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passes through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower boiling reaction components. The stream then entered a two-stage separation and devolatilization system where the polymer was removed from the solvent, hydrogen, and unreacted monomer and comonomer. The separated and devolatilized polymer melt was pumped through a die specially designed for underwater pelletization, cut into uniform solid pellets, dried, and transferred into a box for storage.

EXAMPLES

[00129] One or more features of the present disclosure are illustrated in view of the examples as follows.

[00130] The following catalysts were utilized in one or more of the examples described subsequently in more detail:





[00131] **Example 1: Preparation of Compositions 1–9**

[00132] Multimodal Ethylene-based Polymer Compositions 1–9, which are described according to the one or more embodiments of the detailed description, were prepared by a process utilizing the catalysts and reactors described below.

[00133] The reactor and feed conditions for the synthesis of Compositions 1–9 are provided in Table 1.

Table 1: Reactor and Feed Conditions for the Synthesis of Compositions 1–9.

Multimodal Ethylene-based Polymer Composition	1	2	3	4	5	6	7	8	9
Reactor Conf.	Single	Single	Single	Single	Single	Single	Single	Single	Single
Comonomer Type	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene
Catalyst 1	A	A	A	A	A	A	A	A	A
Catalyst 2	C	C	D	C	C	D	D	C	C
Catalyst 1 Feed Con. (mmol/kg)	0.025	0.025	0.05	0.025	0.025	0.025	0.025	0.025	0.022
Catalyst 1 Flow (g/hr)	375	375	295	87	86	79	84	82	100
Catalyst 2 Feed Con. (mmol/kg)	0.075	0.075	0.1	0.075	0.075	0.04	0.04	0.075	0.022
Catalyst 2 Flow (g/hr)	75	99	375	22	29	60	100	31	80
Total Solvent Flow (kg/hr)	37	37.1	37.2	33.3	33.3	33.2	33.1	--	14.3
Reactor 1 Temp (°C)	190	190	190	165	165	165	165	165	190
Reactor 1 C2 Feed (kg/hr)	4.72	4.72	4.72	4.5	4.5	1.5	4.5	4.5	2.5

Reactor C8 Feed (kg/hr)	1.3	1.3	1.3	1.53	1.53	1.53	1.53	1.53	0.38
Reactor 1 H2 Feed (sccm)	5	5	5	15	27	15	26	27	145
Reactor 1 Exit [C2] (g/L)	3	3	3	6	6	6	6	6	10
Reactor 1 residence time (min)	4.3	4.3	4.3	4.9	4.9	4.9	4.9	4.9	8.1
Percent solids (%)	13	12	13	13	13	13	13	13	14

[00134] Example 2: Preparation of Comparative Compositions C1–C3

[00135] Comparative Compositions C1–C3 were prepared by a process utilizing the catalysts and reactors described below.

[00136] All raw materials (monomer and comonomer) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent, Isopar-E) were purified with molecular sieves before introduction into the reaction environment. Hydrogen was supplied pressurized as a high purity grade and was not further purified. The reactor monomer feed stream was pressurized via a mechanical compressor to above reaction pressure. The solvent and comonomer feed was pressurized via a pump to above reaction pressure. The individual catalyst components were manually batch diluted with purified solvent and pressured to above reaction pressure. All reaction feed flows were measured with mass flow meters and independently controlled with computer automated valve control systems. The reactor and feed conditions for the synthesis of Comparative Compositions C1–C3 are provided in Table 3.

Table 2: Reactor and Feed Conditions for the Synthesis of Comparative Comp. C1–C3.

Comparative Ethylene-based Polymer Composition	C1	C2	C3
Reactor Conf.	Single	Single	Single
Comonomer Type	1-octene	1-octene	1-octene
Catalyst 1	A	A	A
Catalyst 2	--	--	--
Catalyst 1 Feed Con. (mmol/kg)	0.025	0.025	0.05
Catalyst 1 Flow (g/hr)	125	375	129
Catalyst 2 Feed Con. (mmol/kg)	--	--	--
Catalyst 2 Flow (g/hr)	--	--	--
Total Solvent Flow (kg/hr)	33.4	37	36.8
Reactor 1 Temp (°C)	165	190	179

Reactor 1 C2 Feed (kg/hr)	4.5	4.72	4.72
Reactor C8 Feed (kg/hr)	1.53	1.3	1.15
Reactor 1 H2 Feed (sccm)	15	5	5
Reactor 1 Exit [C2] (g/L)	6	3	3
Residence time (min)	4.9	4.3	4.4
Percent solids (%)	13	13	13

[00137] Example 3: Comparative Compositions C4–C8

[00138] Table 3 identifies the commercially-available Comparative Compositions C4–C8.

Table 3: Commercially-available Comparative Compositions C4–C8.

Comparative Composition	Commercial Name (Company of Manufacture)
C4	Agility 1021 (Dow Chemical Co.)
C5	Agility 1200 (Dow Chemical Co.)
C6	Dowlex 2045 (Dow Chemical Co.)
C7	Innate ST70 (Dow Chemical Co.)
C8	Elite 5400 (Dow Chemical Co.)

[00139] Example 4: Preparation of Comparative Compositions C9–C19

[00140] Comparative Compositions 9–19 were prepared by a process utilizing the catalysts and reactors described below.

Table 5: Reactor and Feed Conditions for the Synthesis of Comparative Comp. C9–C19.

	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19
Reactor Conf.	Dual	Dual	Dual	Dual	Dual	Dual	Dual	Dual	Dual	Dual	Dual
Comonomer Type	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene	1-octene
Reactor 1 Temp (°C)	123	160	160	210	210	210	210	210	210	225	225
Reactor 1 Solvent Feed (kg/h)	20.6	29.8	29.7	15.5	15.5	15.5	15.5	15.8	15.8	15.8	15.8
Reactor 1 C2 Feed (kg/hr)	3.41	1.2	1.2	2.57	2.57	2.57	2.57	2.52	2.52	2.52	2.52
Reactor 1 C8 Feed (kg/hr)	1.01	0.9	0.9	1.2	1.2	1.2	1.2	1.05	1.05	1.05	1.05
Reactor 1 H2 Feed (sccm)	11	0	4	19	19	19	19	4	4	4	4

Reactor 1 Exit [C2] (g/L)	22.2	13	13	2.13	2.13	1.8	1.98	1.82	1.82	2	1.7
Reactor 2 Temp (°C)	190	160	160	170	170	170	170	170	170	170	170
Reactor 2 Solvent Feed (kg/h)	10	19.3	19.6	20.2	20.2	9	9	15.6	15.6	15.5	15.5
Reactor 2 C2 Feed (kg/hr)	2.12	4.7	4.7	3.84	3.84	1.7	1.7	2.96	2.96	2.96	2.96
Reactor 2 C8 Feed (kg/hr)	0.4	0.55	0.35	0.67	0.67	0.1	0.1	0.64	0.62	0.53	0.53
Reactor 2 H2 Feed (sccm)	200	420	270	455	455	260	300	364	310	299	300
Reactor 2 Exit [C2] (g/L)	4.91	13.1	13.2	2.95	2.95	2.7	3.37	2.23	2.23	1.4	1.44
Catalyst 1	E	D	D	F	F	F	F	A	A	A	A
Catalyst 2	--	--	--	--	--	--	--	--	--	--	--
Catalyst 3	B	D	D	C	C	C	C	C	C	C	C
Catalyst 1 Feed Conc. (mmol/kg)	0.34	0	0	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Catalyst 1 Flow (g/hr)	60	186	154	143	143	125	193	144	171	210	200
Catalyst 2 Feed Conc. (mmol/kg)	--	--	--	--	--	--	--	--	--	--	--
Catalyst 2 Flow (g/hr)	--	--	--	--	--	--	--	--	--	--	--
Catalyst 3 Feed Conc. (mmol/kg)	0.02	--	--	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Catalyst 3 Flow (g/hr)	45	--	--	141	141	107	114	123	130	256	270

[00141] Example 5: Analysis of Compositions 1–10 and Comparative Compositions 1–19.

[00142] In Example 5, the Multimodal Ethylene-based Polymer Compositions 1–10 and Comparative Compositions 1–19 were tested for the properties listed in Tables 6–8, according to the test methods described herein.

Table 5: Evaluation of Catalysts A–E in a Semi-Batch Reactor

Catalyst	Reaction Temp. (°C)	Yield (g)	Efficiency (kgPE/gM)	Mw (kg/mol)	1- Octene wt%	1- Octene mol%	Tm (°C)	Reactivity ratio r_1^*	Reactivity ratio r_2^*
A	160	11.7	1,781	38.4	13.5	3.75	104	10.5	0.09
A	190	7.2	526	32.8	12.0	3.3	107	12.0	0.08

D	160	48.2	813	1,695	15.0	4.23	96	9.3	0.11
D	190	13.0	543	570	9.5	2.56	104	15.6	0.06
C	160	40.6	2,275	893	16.7	4.77	87	8.2	0.12
C	190	22.7	339	559	12.7	3.51	96	11.3	0.09
E	160	10.5	110	145	8.0	2.1	110	19.1	0.05

Conditions: 160 °C runs: 320 psi ethylene, 60 g 1-octene, 0 H₂, 1250 mL Isopar E solvent. 190 °C runs: 410 psi ethylene, 65 g 1-octene, 0 H₂, 1250 mL Isopar E solvent. All runs: mol fraction of ethylene in solution = 0.709.

*Reactivity ratio r_1 is the reactivity ratio for a monomer insertion after ethylene, and is calculated using the Mayo-Lewis equation:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

where r_2 is the reactivity ratio for a monomer insertion after the comonomer (here 1-octene), f_1 is the mol fraction of ethylene in the feed, f_2 is the mol fraction of comonomer (1-octene) in the feed, and F_1 is the mol fraction of ethylene in the polymer.

$$F_1 = 1 - F_2$$

where F_2 is the mol fraction of 1-octene in the polymer. This value can be obtained experimentally by GPC analysis of the polymer.

The Mayo-Lewis equation can be solved using the GRG Nonlinear solving method available in Microsoft Excel to find the r_1 and r_2 values that give the best fit.

[00143] For Catalyst E, 25 g of 1-octene was added along with 1442 g of ISOPAR-E. The reactor was heated to 165 °C., and saturated with ethylene at about 169 psi total reactor pressure. A catalyst solution was prepared by combining solutions of Catalyst E, RIBS-II, and MMAO-3A to give 6 μmoles of Ti, 7.2 μmoles of RIBS-II, and 30 μmoles of Al.

[00144] For Catalyst C and Catalyst D, 1.47 Kg Isopar-E; 100 g octene; 100g ethylene; temperature was 160 °C; total pressure was 410 psi; procatalyst:activator ratio was 1:1.2; activator was [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄]; MMAO-3A was used as an impurity scavenger at a 50:1 molar ratio (Al:procatalyst); reaction time was 10 min. Efficiency (Eff) in units of kilograms of polymer per gram of active metal (Zr or Hf) in the catalyst.

Table 6: Analysis of Compositions 1–10 and Comparative Compositions 1–19.

	Catalyst	Mn* (kDa)	Mw* (kDa)	Mz* (kDa)	Mw/ Mn*	Mz/ Mw**	Mn**	Mw**	Mz**	MW _{(abs)/} MW _(GPC)
C1	A	20.2	64.7	193.4	2.6	2.7	20.3	53.2	141.5	1.21

C2	A	18.7	62.1	160	2.7	2.4	18.8	50.7	121.2	1.21
C3	A	22.7	77.9	185.8	2.8	2.3	22.8	63.2	146.1	1.22
C4	--	12.5	251.4	941.6	8.8	4.8	12.2	107.6	514.1	2.32
C5	--	15	401.9	1075	11.5	4.5	14.4	165.6	738.5	2.42
C6	Ziegler-Natta	24.9	119.6	444.5	4.6	4	26.1	120.6	484.3	0.99
C9	E/B	45.2	111.3	228.4	2.3	2.1	46.1	106.8	219.5	1.04
C10	D/D	33.1	118.1	1095	3.7	13.6	33.3	124.5	1692	0.96
C11	D/D	50	136.4	645.7	2.8	6.4	48.6	135.8	874.4	1
C12	F/C	27.2	89	299.1	2.8	2	25.6	72.6	147.2	1.23
C13	F/C	28.7	88.8	280.6	2.8	2	25.5	72.1	143.2	1.23
C14	F/C	25.4	93.4	348.6	3.1	2.2	24	75.2	162.3	1.24
C15	F/C	26.3	89.1	310	2.9	2.1	24.2	70.9	146.6	1.26
C16	A/C	20.8	87.3	237.7	3.5	2	19.6	68.5	139.8	1.27
C17	A/C	20	89.9	242	3.7	2.1	18.9	70.1	149	1.28
C18	A/C	20.6	88.4	208.1	3.5	2	20.1	69.8	138.8	1.27
C19	A/C	22.6	88.1	200.6	3.3	2	21	69.8	136.7	1.26
1	A/C	20.4	85.2	327.6	3.5	4.3	19.9	69.2	299.8	1.23
2	A/C	20.1	98.4	429.5	4	5.2	20.4	81.5	421.5	1.21
3	A/D	21	83.7	242.5	3.3	3.3	21.3	70.2	229.5	1.19
4	A/C	21.6	90.5	529.2	3.5	6.6	21.4	75.3	499	1.2
5	A/C	20.4	99.5	628.3	4.1	7.1	20.2	82.5	584.7	1.2
6	A/D	22	82.5	360.5	3.3	4.8	21.4	71.1	342.1	1.16
7	A/D	20.8	83.9	339.7	3.4	4.3	20.8	71	305.2	1.19
8	A/C	20.5	104.2	661.5	4.2	7.2	20.3	85.8	613.9	1.22
9	G/C	29.2	87.8	240.2	3.0	2.7	32.8	87.0	255.6	1.01

*Values from absolute GPC analysis

**Values from conventional GPC analysis

Table 7: Analysis of Compositions 1–9 and Comparative Compositions 1–19.

	Catalyst	C8 wt%	Density (g/cc)	LCBf	V0.1/V100
C1	A	18	0.9058	0.685	4
C2	A	16.4	0.9076	0.767	3.7
C3	A	15.2	0.9095	0.746	9.7
C4	--	--	0.92	1.35	49
C5	--	--	0.919	1.639	21
C6	Ziegler-Natta	8.1	0.92	0.000	5
C7	Molecular	7.9	0.9225	0.045	
C8	Molecular	11.4	0.916	0.077	
C9	E/B	7.1	0.9243	0	4.7
C10	D/D	8.1	0.9197	0	6.2
C11	D/D	6.8	0.9176	0	4.5
C12	F/C	--	0.9048	0.049	15.2
C13	F/C	--	0.9045	0.164	14.8
C14	F/C	--	0.9049	0.138	19.6

C15	F/C	--	0.9043	0.196	15.4
C16	A/C	--	0.9041	0.192	17.0
C17	A/C	--	0.9044	0.173	19.3
C18	A/C	--	0.9035	0.071	18.6
C19	A/C	--	0.9038	0.155	16.4
1	A/C	16.3	0.9078	0.828	16
2	A/C	16.2	0.908	0.727	22
3	A/D	16.2	0.9075	0.786	18
4	A/C	17.5	0.9065	0.547	12
5	A/C	17.6	0.905	0.568	17
6	A/D	17.4	0.9053	0.606	14
7	A/D	17.4	0.9066	0.535	18
8	A/C	17.5	0.9065	0.538	16
9	G/C	0.0	0.9516	0.006	4.8

Table 8: Analysis of Compositions 1–10 and Comparative Compositions 1–19.

	Catalyst	CDF LS 500,000 g/mol cutoff %	Melt strength (cN)	Drawability (mm/s)	Activation Energy (kJ/mol)	Vinyl end group count per 1000 C	MI	I10/I2
C1	A	7.3	2.7	243	49	--	6.5	10.7
C2	A	5.7	1.3	259	50	0.545	8.0	10.4
C3	A	5.2	4.3	221	53	0.464	1.8	12.8
C4	--	53.2	8.0	230	52	--	1.85	14.5
C5	--	62.8	22.0	60	48	--	0.23	17.3
C6	Ziegler-Natta	24.5	3.2	215	30	--	1.0	8.2
C7	Molecular	16.1	4.1	207.5	33.2		0.85	8
C8	Molecular	13.9	4.1	164.0	36.3		1.0	8.5
C9	E/B	7.1	4.3	181	32	0.036	0.86	7.1
C10	D/D	44.0	2.2	150	33.3	0.012	3.68	6.8
C11	D/D	28.9	3.9	196	31.0	0.018	0.99	6.7
C12	F/C	4.78	4.1	253	49.6	0.112	0.80	14.3
C13	F/C	4.96	4.2	240	49.9	0.11	0.85	14.2
C14	F/C	6.18	5.3	232	53.4	0.156	0.62	16.1
C15	F/C	5.18	4.4	254	53.3	0.14	0.91	14.8
C16	A/C	2.75	5.3	259	54.4	0.249	0.94	15.3
C17	A/C	3.69	5.3	260	55.1	0.293	0.90	16.0
C18	A/C	2.13	5.7	266	54.4	0.225	0.69	15.8
C19	A/C	2.12	6.2	266	54.3	0.190	0.77	15.3
1	A/C	20.5	19.5	125	51	0.521	1.92	14.6
2	A/C	27.8	26.5	96	52	0.520	0.9	19.0
3	A/D	11.0	11.1	163	52	0.485	1.03	16.1
4	A/C	31.2	34.0	49	50	0.512	1.85	13.7
5	A/C	39.5	32.6	53	49	0.514	1.68	14.8
6	A/D	22.7	16.5	107	50	0.496	1.71	14.9

7	A/D	22.2	11.7	131	50	0.495	1.74	15.5
8	A/C	41.6	36.0	52.0	47	0.505	1.45	11.1
9	G/C	14	4.5	164	29	0.494	3.9	6.9

[00145] As shown in Tables 6–8, Samples 1–10 exhibited improved melt strength in comparison to Comparative Samples C1–C19. C1–C3, C9, and C12–C19 all failed to exhibit enough high molecular weight fraction, computed by the area fraction of the MWD greater than 500,000 g/mol as obtained by absolute molecular weights from GPC light scattering analysis. Additionally, Comparative Samples C4–C5 exhibited a high molecular weight fraction of greater than 50% of the area fraction of the MWD greater than 500,000 g/mol as obtained by absolute molecular weights from light scattering. Additionally, Samples 1–10 exhibited higher amount of vinyl end groups per 1000 carbon atoms when compared to Comparative Examples C12–C19. The increase in the number of vinyl end group count correlates to the increase in long chain branching frequency. Additionally, Samples 1–10 exhibited I₁₀/I₂ (melt flow ratio) comparable to or higher than the I₁₀/I₂ of C1–C19, which is indicative of the resin's comparable or improved processability, respectively. Long chain branching is present in both Samples 1–8 and Comparative Samples C1–C3) in comparable quantities; however, only Samples 1–8, having high molecular weight component described herein, exhibited improved melt strength and melt flow ratio. Similarly, both Samples 1–8 and Comparative Samples C1 – C3 have similar LCBf, but only Samples 1–8, having high molecular weight component described herein, exhibited improved melt strength.

CLAIMS

1. A process of polymerizing a multi-modal polyethylene polymer, the process comprising:
contacting ethylene and optionally one or more α -olefin monomers with at least two
catalyst systems in a solution reactor at a reactor temperature of greater than
150°C;
wherein:
the at least two catalyst systems produce a vinyl end group count per 1000 carbon
atoms is greater than 0.3, wherein the vinyl end group count per 1000
carbon atoms is measured by 600 MHz nuclear magnetic resonance
(NMR) instrument;
a first catalyst system of the at least two catalyst systems comprises a first
procatalyst; and
a second catalyst system of the at least two catalyst systems comprises a second
procatalyst having a reactivity ratio of less than 20, wherein the reactivity
ratio of the first procatalyst is measured in a single reactor with only the
first catalyst system in the presence of 1250 grams of ISOPAR-E, with a
mol fraction of ethylene in solution of 0.709, and at a reactor temperature
of at least 150°C.
2. The process of claim 1, wherein the at least two catalyst systems are in one reactor.
3. The process of claim 1 or 2, wherein at least 10% of the multimodal polyethylene
polymer is greater than 500 kg/mol.
4. The process of any one of the preceding claims, wherein the solution reactor is a dual
reactor.
5. The process of claim 4, wherein the first reactor comprises a first catalyst system and a
second catalyst system; and the second reactor of the dual reactor comprises a third catalyst
system.

6. The process of claim 4 or claim 5, wherein the first catalyst system comprises a reaction product a first procatalyst and an activator; the second catalyst system comprises a reaction product a second procatalyst and an activator, and a third catalyst system comprises a reaction product a third procatalyst and an activator.
7. The process of claim 6, wherein the first procatalyst is different from the second procatalyst and the second procatalyst is different from the third procatalyst.
8. The process of claim 7, wherein the first procatalyst is different from the third procatalyst.
9. The process of any one of claims 2 to 8, wherein the reactor temperature of the first reactor is greater than 150°C, and the second reactor temperature of an other reactor is less than 150°C.
10. The process of claim 1, wherein the solution reactor is a single reactor.
11. The process of claim 10, wherein the single reactor has a reactor temperature of greater than 160°C.
12. The process of any one of claims 9 to 11, wherein the vinyl end group count per 1000 carbon atoms is greater than 0.40 when measured 600 MHz nuclear magnetic resonance (NMR) instrument.
13. The process of any one of claims 9 to 11, wherein the vinyl end group count per 1000 carbon atoms is greater than 0.45 when measured 600 MHz nuclear magnetic resonance (NMR) instrument.
14. The process of any one of the preceding claims, wherein the α -olefin monomer is not a diene.

15. The process of any one of claims 1 to 12, wherein the α -olefin monomer comprises a single vinyl group.
16. The process of any one of the preceding claims, wherein the α -olefin monomer is linear.
17. The process of any one of the preceding claims, wherein the α -olefin monomer is a (C₃–C₁₂) α -olefin monomer.
18. The process of anyone of the preceding claims, wherein the at least two catalyst systems comprises at least one co-catalyst.