TRIMODAL ETHYLENE-BASED POLYMER COMPOSITION AND CATALYST SYSTEM

BACKGROUND

[0001] Known are single gas-phase reactor bimodal technologies for the synthesis of olefin terpolymers (ethylene/α-olefins in particular) polymerized with a high molecular weight component and a low molecular weight component. Multimodal polymers, and trimodal polymers in particular, have become increasingly important in the polyolefins industry.

[0002] Consequently, the art recognizes the need for multimodal (and trimodal in particular) olefin-based polymer (and ethylene/α-olefin polymers in particular) synthesis in a single gas-phase reactor with improved comonomer distribution among low molecular weight components that have greater ethylene selectivity.

SUMMARY

[0003] The present disclosure provides a catalyst system. In an embodiment, the catalyst system includes a bimodal catalyst (BMC) spray-dried to a support and a trim catalyst. The trim catalyst includes a phenoxy imine catalyst selected from (i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl and (ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride. The catalyst system also includes at least one spray-dried methylaluminoxane activator.

[0004] The present disclosure also provides a process. In an embodiment, the process includes polymerizing ethylene with one or more α-olefins, under polymerization conditions, with a catalyst system. The catalyst system includes, a bimodal catalyst (BMC) spray-dried to a support and a trim catalyst. The trim catalyst includes a phenoxy imine catalyst selected from (i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl and (ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride. The catalyst system also includes at least one spray-dried methylaluminoxane activator. The process includes forming a trimodal ethylene/α-olefin terpolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1 is a graph showing a plot of dW/dLog(MW) on the y-axis versus Log(MW) on the x-axis for comparative sample 1, inventive example 1, and inventive example 2.

DEFINITIONS

[0006] Any reference to the Periodic Table of Elements is that as published by CRC Press, Inc., 1990–1991. Reference to a group of elements in this table is by the new notation for numbering groups.

[0007] For purposes of United States patent practice, the contents of any referenced patent, patent application or publication are incorporated by reference in their entirety (or its equivalent US version is so incorporated by reference) especially with respect to the disclosure of definitions (to the extent not inconsistent with any definitions specifically provided in this disclosure) and general knowledge in the art.

[0008] The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges containing explicit values (e.g., 1 or 2; or 3 to 5; or 6; or 7), any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.).

[0009] Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight and all test methods are current as of the filing date of this disclosure.

[0010] "Bimodal," as used herein, refers to two, and only two, modalities, or modes.

[0011] A "bimodal catalyst system" ("BMC") is a catalyst system that contains two different catalysts for catalyzing the same polymerization process (e.g., olefin polymerization) and producing a bimodal polymer composition.

[0012] A "catalyst" is a material that enhances rate of a reaction (e.g., the polymerization of ethylene and α-olefin, for example) and is not completely consumed thereby.

[0013] A "catalyst system" is a combination of a catalyst per se and a companion material such as a modifier compound for attenuating reactivity of the catalyst, a support

material on which the catalyst is disposed, a carrier material in which the catalyst is disposed, or a combination of any two or more thereof, or a reaction product of a reaction thereof.

[0014] The term "composition" refers to a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

[0015] The terms "comprising," "including," "having" and their derivatives, are not intended to exclude the presence of any additional component, step, or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step, or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step, or procedure not specifically delineated or listed. The term "or," unless stated otherwise, refers to the listed members individually as well as in any combination. Use of the singular includes use of the plural and vice versa.

[0016] An "ethylene-based polymer" or "ethylene polymer" is a polymer that contains a majority amount, or greater than 50 mol%, of polymerized ethylene based on the weight of the polymer, and, optionally, may comprise at least one comonomer.

[0017] An "ethylene/α-olefin interpolymer" is an interpolymer that contains a majority amount of polymerized ethylene, based on the mole percent of the interpolymer, and at least one α-olefin.

[0018] A "feed" is a quantity of reactant or reagent that is added or "fed" into a reactor. In continuous polymerization operation, each feed independently may be continuous or intermittent. The quantities or "feeds" may be measured, e.g., by metering, to control amounts and relative amounts of the various reactants and reagents in the reactor at any given time.

[0019] A "feed line" is a pipe or conduit structure for transporting a feed.

[0020] A "hydrocarbon " is a compound that contains only hydrogen and carbon atoms. The hydrocarbon can be (i) branched or unbranched, (ii) saturated or unsaturated (iii) cyclic or

acyclic, and (iv) any combination if (i)–(iii). Nonlimiting examples of hydrocarbons include alkanes, alkenes, and alkynes.

[0021] An "interpolymer" (or "terpolymer") is a polymer prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers (employed to refer to polymers prepared from two different types of monomers), terpolymers (employed to refer to polymers prepared from three different types of monomers), and polymers prepared from more than three different types of monomers.

[0022] A "metallocene catalyst" is a homogeneous or heterogeneous material that contains a cyclopentadienyl ligand-metal complex and enhances olefin polymerization reaction rates. Substantially single site or dual site. Each metal is a transition metal Ti, Zr, or Hf. Each cyclopentadienyl ligand independently is an unsubstituted cyclopentadienyl group or a hydrocarbyl-substituted cyclopentadienyl group. In some aspects the metallocene catalyst has two cyclopentadienyl ligands, and at least one, alternatively both of the cyclopentenyl ligands independently is a hydrocarbyl-substituted cyclopentadienyl group. Each hydrocarbyl-substituted cyclopentadienyl group may independently have 1, 2, 3, 4, or 5 hydrocarbyl substituents. Each hydrocarbyl substituent may independently be a ($C_1 - C_4$) alkyl. Two or more substituents may be bonded together to form a divalent substituent, which with carbon atoms of the cyclopentadienyl group may form a ring.

[0023] An "olefin-based polymer" or "polyolefin" is a polymer that contains a majority amount, or greater than 50 mol%, of polymerized olefin monomer, for example, ethylene or propylene, (based on the weight of the polymer), and optionally, may contain at least one comonomer. Nonlimiting examples of an olefin-based polymer include an ethylene-based polymer and a propylene-based polymer.

[0024] A "polymer" is a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term "homopolymer" (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term "interpolymer." A "copolymer" is a polymer having two polymer units that are different from each other. A "terpolymer" is a polymer having three or more polymer

units that are different from each other. "Different" in reference to polymer units indicates that the polymer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. As used herein a "polymerization process" is a process that is utilized to make a polymer. For instance, the polymerization process can be a gas-phase or slurry-phase polymerization process. In some embodiments, the polymerization process consists of a gas-phase polymerization process. In some embodiments the polymerization process consists of a slurry-phase polymerization process. Trace amounts of impurities, for example, catalyst residues, may be incorporated into and/or within the polymer. It also embraces all forms of copolymer, e.g., random, block, etc. The terms "ethylene/α-olefin polymer" and "propylene/α-olefin polymer" are indicative of copolymer as described above prepared from polymerizing ethylene or propylene respectively and one or more additional, polymerizable α-olefin monomer. It is noted that although a polymer is often referred to as being "made of" one or more specified monomers, "based on" a specified monomer or monomer type, "containing" a specified monomer content, or the like, in this context the term "monomer" is understood to be referring to the polymerized remnant of the specified monomer and not to the unpolymerized species. In general, polymers herein are referred to as being based on "units" that are the polymerized form of a corresponding monomer.

[0025] A "trim catalyst" is a quantity of a catalyst that is used in combination with the bimodal catalyst to create the resultant trimodal catalyst system. Trim catalyst is usually fed (e.g., to the GPP reactor) as a solution of the catalyst dissolved in an inert liquid (non-polar, aprotic, e.g., a hydrocarbon solvent such as hexane). The trim catalyst is used with the trimodal catalyst system to modify at least one property of the copolymer composition made thereby. Nonlimiting examples of properties modified by the trim catalyst include density, melt index I_2, flow index I_{21}, melt flow ratio, molecular mass dispersity (M_w/M_n), and any combination thereof.

[0026] "Trimodal," as used herein, refers to three, and only three, modalities, or modes.

[0027] A "trimodal catalyst system" is a catalyst system that contains three different catalysts for catalyzing the same polymerization process (*e.g.*, olefin polymerization) and

producing a trimodal polymer composition. Catalysts are different if they differ from each other in at least one of the following characteristics: (a) their catalytic metals are different (Ti versus Zr, Zr versus Hf, Ti versus Hf; not activator metals such as Al); (b) one catalyst has a functional ligand covalently bonded to its catalytic metal and the other catalysts are free of functional ligands bonded to its catalytic metal; (c) the catalysts have functional ligands covalently bonded to their catalytic metal and the structures of at least one of functional ligand of one of the catalysts is different than the structure of each of the functional ligand(s) of the other catalyst (e.g., cyclopentadienyl versus propylcyclopentadienyl or butylcyclopentadienyl versus (pentamethylphenylamido)ethyl)- amine); and (d) for catalysts disposed on a support material, the compositions of the support materials are different. Functional ligands do not include leaving groups X as defined later. As described herein two catalysts, *i.e.*, the bimodal catalysts contained within the trimodal catalyst system may be disposed on the same support material, either on the same particles of the same support material or each on different particles of the same support material.

[0028] A "trimodal polymer composition" (e.g., a trimodal ethylene/olefin terpolymer composition) is a polymer composition that contains three polymer (polyethylene) fractions (or modes) that have been produced under different polymerization conditions, including differences in any process conditions and/or catalyst systems, resulting in different molecular weights and/or different comonomer contents for the each of the three fractions. For example, each of the three polyethylene fractions may be made by three different respective catalysts, the three catalysts are different in catalytic metal and/or ligand composition. The trimodal polymer composition may be characterized by at least two peaks separated by a distinguishable local minimum therebetween in a plot of dW/dlog(MW) on the y-axis versus Log(MW) on the x-axis to give a Gel Permeation Chromatograph (GPC) chromatogram, wherein Log(MW) and dW/dlog(MW) are as defined herein and are measured by Gel Permeation Chromatograph (GPC) Test Method described herein.

DETAILED DESCRIPTION

[0029] The present disclosure provides a catalyst system. In an embodiment, the catalyst system includes a bimodal catalyst ("BMC") spray-dried to a support. The catalyst system also includes a trim catalyst. The trim catalyst includes a phenoxy imine catalyst selected from (i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl ("FI-A") and/or (ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride ("FI-B"). The catalyst system also includes at least one spray-dried methylaluminoxane activator.

[0030] The catalyst system (interchangeably referred to as "trimodal catalyst system") includes the bimodal catalyst (BMC). The BMC includes (i) a non-metallocene catalyst and (ii) a metallocene catalyst. In an embodiment, the non-metallocene catalyst is bis(2-pentamethylphenylamido)ethyl)-amine zirconium dibenzyl (interchangeably referred to as "Formula III") and (ii) the metallocene catalyst is selected from (i) methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl (interchangeably referred to as "Formula IV"), (ii) η5-cyclopentadienyl)(η5-1,5-dimethylindenyl)dimethylzirconium (interchangeably referred to as "Formula V"), and/or (iii) bis(n-butylcylcopentadienyl)zirconium dimethyl (interchangeably referred to as "Formula VI").

[0031] The BMC is spray-dried to a support. The support may be a porous support material, for example, talc, an inorganic oxide, or an inorganic chloride. Other support materials include resinous support materials, e.g., polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

[0032] Support materials include inorganic oxides that include Group 2, 3, 4, 5, 13 or 14 metal oxides. Some preferred supports include silica, fumed silica, alumina, silica-alumina, and mixtures thereof. Some other supports include magnesia, titania, zirconia, magnesium chloride, montmorillonite, phyllosilicate, zeolites, talc, clays) and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica- alumina, silica-titania and the like. Additional support materials may include porous acrylic polymers, nanocomposites, aerogels, spherulites, and polymeric beads.

[0033] A nonlimiting example of a support is fumed silica available under the trade name CabosilTM TS- 610, or other TS- or TG-series supports, available from Cabot Corporation.

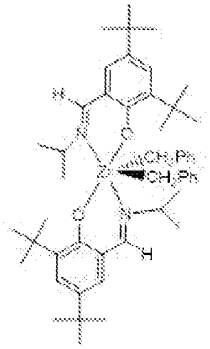
Fumed silica is typically a silica with particles 7 to 30 nanometers in size that has been treated with dimethylsilyldichloride such that a majority of the surface hydroxyl groups are capped.

[0034] In an embodiment, the support material has a surface area in the range from 10 m^2/g to 700 m^2/g, a pore volume in the range from 0.1 g/cm^3 to 4.0 g/cm^3 and an average particle size in the range from 5 to 500 microns. In a further embodiment, the support material has a surface area from 50 to 500 m^2/g, a pore volume from 0.5 to 3.5 g/cm^3 and an average particle size of from 10 microns to 200 mircrons. In yet a further embodiment, the support material has a surface area range from 100 to 400 m^2/g, a pore volume from 0.8 to 3.0 g/cm^3 and an average particle size is from 5 microns to 100 microns. The support material typically has pore size in the range of from 10 angstroms (A) to I000A, or from 50 to 500A, or from 75 to 350A.

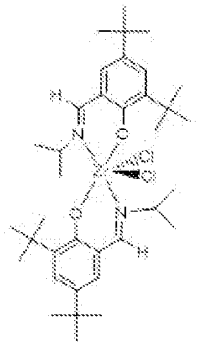
[0035] The BMC is spray-dried onto the support prior to the BMC being contacted with the activator. The solid support may be an uncalcined material or a calcined material prior to being contacted with the BMC. The solid support material may be a hydrophobic fumed silica (e.g., a fumed silica treated with dimethyldichlorosilane). The BMC spray-dried to the support may be in the form of a powdery, free-flowing particulate solid.

[0036] In an embodiment, the BMC is spray-dried to a hydrophobic fumed silica support.

[0037] The catalyst system includes the trim catalyst in addition to the BMC (and activator). The trim catalyst is a phenoxy imine catalyst. The phenoxy imine catalyst is selected from (i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl ("FI-A") having the Formula I below and/or (ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride ("FI-B") having the Formula II as shown below.



(Formula I)



(Formula II)

[0038] The catalyst system also includes an activator. As used herein, "activator" refers to any compound or combination of compounds, supported, or unsupported, which can activate a complex or a catalyst component, such as by creating a cationic species of the catalyst component. For example, this can include the abstraction of at least one leaving group, e.g., from the zirconium metal center of the complex/catalyst component, e.g., the metal complex of Formula I and/or Formula II. As used herein, "leaving group" refers to one or more chemical moieties bound to a metal atom and that can be abstracted by an activator, thus producing a species active towards olefin polymerization.

[0039] The activator can include a Lewis acid or a non-coordinating ionic activator or ionizing activator, or any other compound including Lewis bases, aluminum alkyls, and/or conventional-type co-catalysts. In addition to methylaluminoxane ("MAO") and modified methylaluminoxane ("MMAO"), illustrative activators can include, but are not limited to, aluminoxane or modified aluminoxane, and/or ionizing compounds, neutral or ionic, such as dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis(3,5-$(CF_3)_2$phenyl)borate, triphenylcarbenium tetrakis(3,5-$(CF_3)_2$phenyl)borate, dimethylanilinium tetrakis(perfluoronapthyl)borate, triphenylcarbenium tetrakis(perfluoronapthyl)borate, dimethylanilinium tetrakis(pentafluorophenyl)aluminate, triphenylcarbenium tetrakis(pentafluorophenyl)aluminate, dimethylanilinium tetrakis(perfluoronapthyl)aluminate, triphenylcarbenium tetrakis(perfluoronapthyl)aluminate, a tris(perfluorophenyl)boron, a

tris(perfluoronaphthyl)boron, tris(perfluorophenyl)aluminum, a tris(perfluoronaphthyl)aluminum or any combinations thereof.

[0040] Aluminoxanes can be described as oligomeric aluminum compounds having -Al(R)-O- subunits, where R is an alkyl group. Aluminoxanes can be produced by the hydrolysis of the respective trialkylaluminum compound. MMAO can be produced by the hydrolysis of trimethylaluminum and a higher trialkylaluminum, such as triisobutylaluminum. There are a variety of known methods for preparing aluminoxane and modified aluminoxanes. The aluminoxane can include a modified methyl aluminoxane ("MMAO") type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylaluminoxane type 3A, discussed in U.S. Patent No. 5,041,584). A source of MAO can be a solution having from about 1 wt. % to about a 50 wt. % MAO, for example. Commercially available MAO solutions can include the 10 wt. % and 30 wt. % MAO solutions available from Albemarle Corporation, of Baton Rouge, La.

[0041] One or more organo-aluminum compounds, such as one or more alkylaluminum compound, can be used in conjunction with the aluminoxanes. Examples of alkylaluminum compounds include, but are not limited to, diethylaluminum ethoxide, diethylaluminum chloride, diisobutylaluminum hydride, and combinations thereof. Examples of other alkylaluminum compounds, e.g., trialkylaluminum compounds include, but are not limited to, trimethylaluminum, triethylaluminum ("TEAL"), triisobutylaluminum ("TiBAl"), tri-n-hexylaluminum, tri-n-octylaluminum, tripropylaluminum, tributylaluminum, and combinations thereof.

[0042] In an embodiment, the catalyst system also includes at least one spray-dried methylaluminoxane activator.

[0043] In an embodiment, the trim catalyst is present in an amount from 0.01 wt% to 1.5 wt%, or from 0.04 wt% to 1.3 wt%, or from 0.5 wt% to 1.2 wt%, or 1.0 wt% in a hexane solvent, wherein weight percent is based on the total weight of the catalyst and solvent.

[0044] In an embodiment, the phenoxy imine catalyst is unsupported.

[0045] In an embodiment, the BMC is spray-dried to a fused silica.

Process

[0046] The present disclosure provides a process. In an embodiment, the process includes polymerizing ethylene with one or more olefins, or α-olefins, under polymerization conditions, with a catalyst system composed of (i) BMC spray-dried to a support, and (ii) a trim catalyst. The trim catalyst is a phenoxy imine catalyst selected from (i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl and/or (ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride. The catalyst system also includes at least one spray-dried methylaluminoxane activator. The process includes forming a trimodal ethylene/olefin terpolymer.

[0047] The term "polymerization conditions," as used herein, refers to a combination of variables that may affect a polymerization reaction in a fluidized bed, gas-phase polymerization reactor ("FB-GPP reactor") or a composition or property of a trimodal copolymer composition product made thereby. The variables may include reactor design and size, catalyst composition and amount; reactant composition and amount; molar ratio of different reactants; presence or absence of feed gases such as H_2 and/or O_2, molar ratio of feed gases versus reactants, absence or concentration of interfering materials (e.g., H_2O), absence or presence of an induced condensing agent (ICA), average polymer residence time in the reactor, partial pressures of constituents, feed rates of monomers, reactor bed temperature (e.g., fluidized bed temperature), nature or sequence of process steps, time periods for transitioning between steps. Variables other than that/those being described or changed by the method or use may be kept constant.

[0048] The present polymerization conditions utilize a gas-phase polymerization (GPP) reactor, such as a stirred-bed gas phase polymerization reactor (SB-GPP reactor) or a fluidized-bed gas- phase polymerization reactor (FB-GPP reactor), to make the trimodal polymer composition. For example, the FB-GPP reactor/method may be as described in US 3,709,853; US 4,003,712; US 4,01 1 ,382; US 4,302,566; US 4,543,399; US 4,882,400; US 5,352,749; US 5,541 ,270; EP-A-0 802 202; and Belgian Patent No. 839,380. These SB-GPP and FB-GPP polymerization reactors and processes either mechanically agitate or fluidize by continuous flow of gaseous monomer and diluent the polymerization medium inside the reactor,

respectively. Other useful reactors/processes contemplated include series or multistage polymerization processes such as described in US 5,627,242; US 5,665,818; US 5,677,375; EP-A-0 794 200; EP-B1 -0 649 992; EP-A-0 802 202; and EP-B-634421.

[0049] In operating the present polymerization conditions the following variables can be adjusted and/or controlled in a GPP, SB-GPP, or FB-GPP. Individual flow rates of ethylene ("C_2"), hydrogen ("H_2") and 1 -hexene ("C_6") are controlled to maintain a fixed comonomer to ethylene monomer gas molar ratio (C_6/C_2) equal to a desired value, a constant hydrogen to ethylene gas molar ratio ("H_2/C_2") equal to a desired value, and a constant ethylene ("C_2") partial pressure equal to a desired value. Concentrations of gases are measured by an in-line gas chromatograph to maintain the composition in the recycle gas stream. A reacting bed of growing polymer particles is maintained in a fluidized state by continuously flowing a make-up feed and recycle gas through the reaction zone. The FB-GPP reactor is operated at a total pressure from 2068 kilopascals (kPa) to 2413 kPa (300 to 350 pounds per square inch-gauge (psig)) and at a described first reactor bed temperature RBT. The fluidized bed is maintained at a constant height by withdrawing a portion of the bed at a rate equal to the rate of production of particulate form of the trimodal ethylene/olefin terpolymer composition, which production rate may be from 10 to 90,000 kilograms per hour (kg/hr). The product trimodal ethylene/olefin terpolymer composition is removed semi-continuously via a series of valves into a fixed volume chamber, wherein the removed trimodal ethylene/olefin terpolymer composition is purged to remove entrained hydrocarbons and treated with a stream of humidified nitrogen (N_2) gas to deactivate any trace quantities of residual catalyst.

[0050] In an embodiment, the polymerization conditions include a gas-phase polymerization reactor and the process includes controlling, or otherwise adjusting one, some, or all of the following variables:

(i) a reaction temperature from 75°C to 110°C, or from 75°C to 105°C, or from 90°C to 100°C and/or

(ii) a molar ratio of the hydrogen gas to the ethylene from 0.0003 to 0.0060, or 0.0010 to 0.0050, or from 0.0030 to 0.0045, and/or

(iii) a molar ratio of the α-olefin to the ethylene from 0.0005 to 0.040, or from 0.003 to 0.02, or from 0.0040 to 0.0070, and/or

(iv) a reactor residence time from 1.5 hours to 4.5 hours or from 2.0 hours to 2.9 hours.

[0051] In some embodiments the FB-GPP reactor is a commercial scale reactor such as a UNIPOL™ reactor or UNIPOL™ II reactor, which are available from Univation Technologies, LLC, a subsidiary of The Dow Chemical Company, Midland, Michigan, USA.

[0052] The polymerization conditions may further include one or more additives such as a chain transfer agent or a promoter. The chain transfer agent may be an alkyl metal such as diethyl zinc. Promoters are known such as in US 4,988,783 and may include chloroform, $CFCl_3$, trichloroethane, and difluorotetrachloroethane. Prior to reactor start up, a scavenging agent may be used to react with moisture and during reactor transitions a scavenging agent may be used to react with excess activator. Scavenging agents may be a trialkylaluminum. Gas phase polymerizations may be operated free of (not deliberately added) scavenging agents. The polymerization conditions for gas phase polymerization reactor/method may further include an amount (e.g., 0.5 to 200 ppm based on all feeds into reactor) of a static control agent and/or a continuity additive such as aluminum stearate or polyethyleneimine. The static control agent may be added to the FB- GPP reactor to inhibit formation or buildup of static charge therein.

[0053] In an embodiment, the process includes contacting the activator with the BMC and/or contacting the activator with the trim catalyst. Each contacting step between activator and catalyst independently may be done either (a) in a separate vessel outside the GPP reactor (e.g., outside the FB-GPP reactor), (b) in a feed line to the GPP reactor, and/or (c) inside the GPP reactor (in situ). In option (a) the trimodal catalyst system, once its catalysts are activated, may be fed into the GPP reactor as a slurry in a non-polar, aprotic (hydrocarbon) solvent. In option (c) the trimodal catalyst system may be fed into the reactor prior to activation via a first feed line, the first activator may be fed into the reactor via a second feed line, the trim catalyst may be fed into the reactor via a third feed line, and the second activator may be fed into the reactor via a fourth feed line. Any two of the first to fourth feed lines may be the same or different. The activator(s) may be fed into the reactor in "wet mode" in the form of a solution thereof in an inert liquid such as mineral oil or toluene, in slurry mode as a suspension, or in dry mode as a

powder. Each contacting step may be done in separate vessels, feed lines, or reactors at the same or different times, or in the same vessel, feed line, or reactor at different times, to separately give the bimodal catalyst system and trim catalyst. Alternatively, the contacting steps may be done in the same vessel, feed line, or reactor at the same time to give a mixture of the bimodal catalyst system and trim catalyst *in situ*.

[0054] The process includes polymerizing, or otherwise contacting, ethylene with one or more olefins (or α-olefins), under polymerization conditions, with the trimodal catalyst system. As used herein, an "olefin," refers to a linear, branched, or cyclic compound including carbon and hydrogen and having at least one double bond. As used herein, when a polymer or copolymer is referred to as comprising, e.g., being made from, an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an ethylene content of 75 wt% to 85 wt%, it is understood that the polymer unit in the copolymer is derived from ethylene in the polymerization reaction and the derived units are present at 75 wt% to 85 wt%, based upon the total weight of the polymer. A higher α-olefin refers to an α-olefin having 3 or more carbon atoms.

[0055] In an embodiment, the one or more olefins include one or more α-olefins. Nonlimiting examples of suitable α-olefins include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 3,5,5-trimethyl-1-hexene, and any combination thereof.

[0056] The process includes forming a trimodal ethylene/olefin terpolymer. Examples of nonlimiting examples of trimodal ethylene/olefin terpolymer include trimodal ethylene-based polymers, having at least 50 wt% ethylene, including ethylene-1-butene, ethylene-1-hexene, and ethylene-1-octene copolymers, among others. Other olefins that may be utilized include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins, for example. Examples of the monomers may include, but are not limited to, norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene. In a number of embodiments, a copolymer of ethylene can be produced, where with ethylene, a comonomer having at least one α-olefin having from 4 to 15 carbon atoms, or from 4 to 12 carbon atoms, or from 4 to 8 carbon atoms, is

polymerized, e.g., in a gas-phase polymerization process. In another embodiment, ethylene and/or propylene can be polymerized with at least two different comonomers, optionally one of which may be a diene, to make a terpolymer. "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0057] One or more embodiments provide that the trimodal ethylene/olefin terpolymer can include from 50 to 99 wt%, or from 51 to 99 wt% of units derived from ethylene based on a total weight of the polymer. All individual values and subranges from 50 to 99 wt% are included; for example, the polymer can include from a lower limit of 50, 51, 60, or 70 wt% of units derived from ethylene to an upper limit of 99, 95, 90, or 85 wt% of units derived from ethylene based on the total weight of the polymer. The polymer can include from 1 to 50 wt%, or from 1 to 49 wt% or from 1 wt% to 25 wt%, or from 1 wt% to 12 wt%, or from 1 wt% to 5 wt% of units derived from comonomer based on the total weight of the polymer.

[0058] As mentioned, surprisingly, the phenoxy imine olefin polymerization catalyst is particularly well adapted to help to provide multimodal polymers and particularly trimodal ethylene/olefin terpolymer via a polymerization process in a gas-phase polymerization reactor in combination with other polymerization catalysts. For instance, the resultant trimodal ethylene/olefin terpolymer can have an improved, i.e., higher, polydispersity index (PDI) as detailed herein, as compared to polymers made with other (non-inventive) polymerization catalysts at similar polymerization conditions. An increased PDI is desirable in some applications. Similarly, the resultant trimodal ethylene/olefin terpolymer can have at least a high molecular weight polyethylene component, a medium molecular weight polyethylene component, and a low molecular weight polyethylene component, as detailed herein. Having a high molecular weight polyethylene component, a medium molecular weight component, and a low molecular weight polyethylene component is desirable in some applications.

[0059] In an embodiment, the trimodal ethylene/α-olefin terpolymer is a trimodal ethylene/hexene copolymer and has one, some or all of the following properties:

(i) a density from 0.930 g/cc to 0.960 g/cc, or from 0.935 g/cc to 0.955 g/cc, or from 0.940 g/cc to 0.950 g/cc; and/or

(ii) a Mn (number average molecular weight) from 10,000 g/mol to 20,000 g/mol, or from 12,000 g/mol to 18,000 g/mol; and/or

(iii) a Mw (weight average molecular weight) from 200,000 g/mol to 275,000 g/mol, or from 225,000 g/mol to 270,000; and/or

(iv) a Mw/Mn from 10.00 to 25.0, or from 12.0 to 20.0; and/or

(v) a Mz (z-average molecular weight) from 500,000 to 3,000,000, or from 750,000 to 2,800,000, or from 2,000,000 g/mol to 2,800,000 g/mol, or from 2,200,000 g/mol to 2,500,000 g/mol; and/or

(vi) a BBF value from 1.1 to 1.7, or from 1.2 to 1.4; and/or

(vii) a vinyl content from 0.20 to 0.60, or from 0.35 to 0.55, or from 0.40 to 0.50 per 1000 carbon; and/or

(viii) a high molecular weight split greater than 55%, or from 56% to 75%, or from 56% to 60%; and/or

(ix) an oligomer content less than 500 ppm, or from 1 ppm to 250 ppm, or from 100 ppm to 250 ppm; and/or

(x) combinations thereof.

[0060] The trimodal ethylene/α-olefin terpolymer can be utilized for a number of articles such as films, fibers, nonwoven and/or woven fabrics, extruded articles, and/or molded articles, among others.

[0061] Some embodiments of the present disclosure will now be described in detail in the following Examples.

TEST METHODS

[0062] Butyl Branch Frequency (BBF): Comonomer content is determined using ^{13}C NMR analysis in accordance with techniques described, for example, in U.S. Patent No. 5,292,845 (Kawasaki, et al.) and by J. C. Randall in Rev. Macromol. Chem. Phys., C29, 201 -317, ranging from homopolymer zero short chain branches per 1,000 total carbon atoms (0 SCB/1000 total C) to 50 SCB/1000 total C, where total C is the sum of the carbons in polymer backbone plus the carbons in all polymer branches. In poly(ethylene-co-1 - hexene) copolymer,

most or all branches are butyl groups (e.g., -$(CH_2)_3CH_3$) and the butyl branch frequency (BBF) equals the number of butyl branches per 1000 total C.

[0063] Differential Scanning Calorimetry (DSC). Melt temperature can be determined via Differential Scanning Calorimetry according to ASTM C 3418-08l. For instance, using a scan rate of 10° C./min on a sample of 10 mg and using the second heating cycle.

[0064] Density is measured according to ASTM D792-13, Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, Method B (for testing solid plastics in liquids other than water, e.g., in liquid 2-propanol). Report results in units of grams per cubic centimeter (g/cc).

[0065] Gel permeation chromatography (GPC) Test Method: Weight-Average Molecular Weight Test Method: determine molecular weight (M_w), number-average molecular weight (M_n), average molecular weight (M_z), and M_w/M_n (PDI) are determined by using chromatograms obtained on a High Temperature Gel Permeation Chromatography instrument (HTGPC, Polymer Laboratories). The HTGPC is equipped with transfer lines, a differential refractive index detector (DRI), and three Polymer Laboratories PLgel 10pm Mixed-B columns, all contained in an oven maintained at 160° C. Method uses a solvent composed of BHT-treated TCB at nominal flow rate of 1.0 milliliter per minute (mL/min.) and a nominal injection volume of 300 microliters (4). Prepare the solvent by dissolving 6 grams of butylated hydroxytoluene (BHT, antioxidant) in 4 liters (L) of reagent grade 1,2,4-trichlorobenzene (TCB), and filtering the resulting solution through a 0.1 micrometer (μm) Teflon filter to give the solvent. Degas the solvent with an inline degasser before it enters the HTGPC instrument. Calibrate the columns with a series of monodispersed polystyrene (PS) standards. Separately, prepare known concentrations of test polymer dissolved in solvent by heating known amounts thereof in known volumes of solvent at 160 °C. with continuous shaking for 2 hours to give solutions. (Measure all quantities gravimetrically.) Target solution concentrations, *c*, of test polymer of from 0.5 to 2.0 milligrams polymer per milliliter solution (mg/mL), with lower concentrations, *c*, being used for higher molecular weight polymers. Prior to running each sample, purge the DRI detector. Then increase flow rate in the apparatus to 1.0 mL/min/ and allow the DRI detector to stabilize for 8 hours before injecting the first sample. Calculate M_w and M_n using universal calibration

relationships with the column calibrations. Calculate MW at each elution volume with following equation:

$$\log M_X = \frac{\log(K_X / K_{PS})}{a_X + 1} + \frac{a_{PS} + 1}{a_X + 1} \log M_{PS}$$

, where subscript "X" stands for the test sample, subscript "PS" stands for PS standards, a_{PS} =0.67, K_{PS} =0.00017:, and a_X and K_X are obtained from published literature. For polyethylenes, a_X/K_X = 0.695/0.000579. For polypropylenes a_X/K_X = 0.705/0.0002288. At each point in the resulting chromatogram, calculate concentration, *c*, from a baseline-subtracted DRI signal I_{DRI}, using the following equation: $C = K_{DRI} I_{DRI}/(dn/dc)$, wherein K_{DRI} is a constant determined by calibrating the DRI, / denotes division and *dn/dc* is the refractive index increment for the polymer. For polyethylene, dn/dc = 0.109. Calculate mass recovery of polymer from the ratio of the integrated area of the chromatogram of concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume. Report all molecular weights in grams per mole (g/mol) unless otherwise noted. Further details regarding methods of determining Mw, Mn, MWD are described in US 2006/0173123 page 24-25, paragraphs [0334] to [0341]. Plot of dW/dLog(MVV) on the y-axis versus Log(MW) on the x-axis to give a GPC chromatogram, wherein Log(MW) and dW/dLog(MVV) are as defined above.

[0066] Comonomer content (i.e., 1-hexene) incorporated in the polymers (weight %) is determined by rapid FT-IR spectroscopy on the dissolved polymer in a GPC measurement. Comonomer content may be determined with respect to polymer molecular weight by use of an infrared detector such as an IR5 detector in a gel permeation chromatography measurement, as described in Analytical Chemistry 2014, 86(17), 8649-8656. "Toward Absolute Chemical Composition Distribution Measurement of Polyolefins by High-Temperature Liquid Chromatography Hyphenated with Infrared Absorbance and Light Scattering Detectors" by Dean Lee, Colin Li Pi Shan, David M. Meunier, John W. Lyons, Rongjuan Cong, and A. Willem deGroot. *Analytical Chemistry 2014 86 (17), 8649-8656.*

[0067] Melt Indices. ("I_2") Test Method: for ethylene-based (co)polymer is measured according to ASTM D1238-13, using conditions of 190° C./2.16 kg. ("I_5") Test Method: for

ethylene-based (co)polymer is measured according to ASTM D1238-13, using conditions of 190° C./5.16 kg. High Load Melt Index ("I_{21}") is measured according to ASTM D1238-13, using conditions of 190° C./21 .6 kilograms (kg). Report results in units of grams eluted per 10 minutes (g/10 min.).

[0068] ^{1}H nuclear magnetic resonance (^{1}H NMR) Test Method: detects the following types of carbon- carbon double bonds ("unsaturation") in the polymer. "Vinyl" is a carbon-carbon double bond with the formula R-CH= CH_2, wherein R is a carbon atom, or a heteroatom selected from N, O, P, B, S, and Si. Polymer samples for ^{1}H NMR analysis were prepared by adding 130 mg of sample to 3.25 g of 50/50 by weight tetrachlorethane-d_2/perchloroethylene with 0.001 M $Cr(AcAc)_3$ in a 10 mm NMR tube. The samples were purged by bubbling N2 through the solvent via a pipette inserted into the tube for approximately 5 minutes to prevent oxidation, capped, sealed with Teflon tape. The samples were heated and vortexed at 115°C to ensure homogeneity. ^{1}H NMR was performed on a Bruker AVANCE 400/600 MHz spectrometer equipped with a Bruker high-temperature CryoProbe and a sample temperature of 120°C. Two experiments were run to obtain spectra, a control spectrum to quantify the total polymer protons, and a double presaturation experiment, which suppresses the intense polymer backbone peaks and enables high sensitivity spectra for quantitation of the end-groups. The control was run with ZG pulse, 4 scans, SWH 10,000 Hz, AQ 1.64s, Di 14s. The double presaturation experiment was run with a modified pulse sequence, Iclprf2.zzl, TD 32768, 100 scans, DS 4, SWH 10,000 Hz, AQ 1.64s, Di Is, D_{i3} 13s. Vinyl content is reported as the number of vinyl bonds per 1000 carbon atoms (1000C).

[0069] HMW Split. The fitting of the chromatogram into a high molecular weight (HMW) and low molecular weight (LMW) component fraction was accomplished using a Flory distribution which was broadened with a normal distribution function as follows:

For the log M axis, 501 equally-spaced Log(M) points, spaced by 0.01, were established between 2 and 7 representing the molecular weight range between 100 and 10,000,000 where Log is the logarithm function to the base 10.

At any given Log (M), the population of the Flory distribution was in the form of Eq. 13:

$$dW_f = \left(\frac{2}{M_w}\right)^3 \left(\frac{M_w}{0.868588961964}\right) M^2 e^{\left(-2M/M_w\right)} \quad Eq.13$$

where Mw is the weight-average molecular weight of the Flory distribution and M is the specific x-axis molecular weight point, (10 ^ [Log(M)]).

[0070] The Flory distribution weight fraction was broadened at each 0.01 equally-spaced log(M) index according to a normal distribution function, of width expressed in Log(M), *s;* and current M index expressed as Log(M), *m*.

$$f_{(LogM,\mu,\sigma)} = \frac{e^{\frac{(LogM-\mu)^2}{2\sigma^2}}}{\sigma\sqrt{2\pi}} \quad Eq.14$$

[0071] It should be noted that before and after the spreading function has been applied that the area of the distribution (dW_f /dLogM) as a function of Log(M) is normalized to unity.

[0072] Two weight-fraction distributions, dW_{f1} and dW_{f2}, for LMW and HMW components or components 1 and 2 were expressed with two unique Mw target values, Mw_1 and Mw_2 and with overall component compositions A_1 and A_2. Both distributions were broadened with the same width, *s*. The two distributions were summed as follows:

$$dW_f = A_1\, dW_{f1} + A_2\, dW_{f2} \quad Eq.15$$

where: $A_1+A_2 = 1$

[0073] The weight fraction result of the measured (from Conventional GPC) GPC molecular weight distribution was interpolated along 501 log M points using a 2nd-order polynomial. Microsoft Excel™ 2010 Solver was used to minimize the sum of squares of residuals for the equally-spaces range of 501 LogM points between the interpolated chromatographically determined molecular weight distribution and the two broadened Flory distribution components ($s_1$and s_2), weighted with their respective component compositions, A_1 and A_2.

The iteration starting values for the components are as follows:

Component 1: Mw = 30,000, *s* = 0.300, and A = 0.475

Component 2: Mw = 250,000, *s* = 0.300, and A = 0.475

(Note $s_1 = s_2$ and $A_1 + A_2 = 1$)

[0074] The bounds for components 1 and 2 are such that s is constrained such that $s > 0.001$, yielding an Mw/Mn of approximately 2.00 and $s < 0.450$, yielding a Mw/Mn of approximately 5.71. The composition, A, is constrained between 0.000 and 1.000. The Mw is constrained between 2,500 and 2,000,000. The composition, A, is constrained between 0.000 and 1.000. The Mw is constrained between 2,500 and 2,000,000.

[0075] The "GRG Nonlinear" engine was selected in Excel Solver™ and precision was set at 0.00001 and convergence was set at 0.0001. The solutions were obtained after convergence (in all cases shown, the solution converged within 60 iterations).

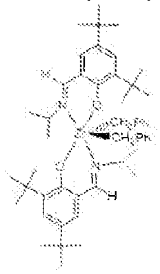
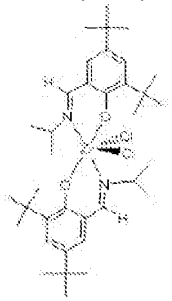
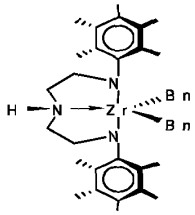
[0076] Determine the respective weight percents (wt%) for each of the LMW and HMW polyethylene components in the inventive trimodal composition by using summed values of the weight fractions (Wf) of the LMW and HMW polyethylene components and the respective number average molecular weights (M_n) and weight average molecular weights (M_w) by known mathematical treatment of aggregated Schulz-Flory MW distributions.

[0077] Oligomer content. Volatile oligomers were determined in polyethylene (PE) using headspace gas chromatography with a flame ionization detector. An aliquot of the headspace vapors from a heated headspace vial containing the sample is analyzed by headspace gas chromatography (HS/GC) with an Agilent model 8697 automated headspace analyzer and an Agilent model 8890 gas chromatograph with a flame ionization detector. About 1 g of resin was added to a headspace vial and sealed. One injection (extraction) was performed from each vial containing the resin after equilibrating for 30 min at 150 °C. Calibration was performed using an external standard calibration procedure with liquid standards covering the volatile oligomer range from 1-hexene to hexadecane (C_6-C_{16}). The liquid standard was spiked onto 1 g of a purged gas phase PE sample in a headspace vial. The standard preparation corrects for partitioning of the components between the headspace and polymer. The data are reported as parts per million (ppm).

[0078] Peak molecular weight ("Mp"). The peak molecular weight ("Mp") is the Mw at the peak top inflection point for each peak in FIG. 1. The peak molecular weight for the low molecular

weight peak ("Mp LMW") is the Mw at the peak top inflection point for the low peak in FIG. 1. The high molecular weight peak ("Mp HMW") is the Mw at the peak top inflection point for the low peak in FIG. 1 . The "Spread" is the difference between the Mp HMW and the Mp LMW.

[0079] Table 1A - Catalysts

Catalyst	Chemical name
phenoxy imine olefin polymerization catalyst of Formula I ("FI-A")  (Formula I)	bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl ("FI-A")
phenoxy imine olefin polymerization catalyst of Formula II ("FI-B")  (Formula II)	bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride ("FI-B")
Non-metallocene catalyst of Formula III  (Formula III)	bis (2-pentamethylphenylamido)ethyl)-amine zirconium dibenzyl)
Metallocene catalyst of Formula IV	methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl

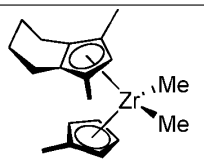
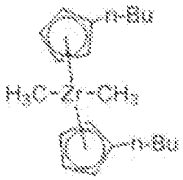
 (Formula IV)	
Metallocene catalyst of Formula V  (Formula V)	η5-cyclopentadienyl)(η5-1,5-dimethylindenyl)dimethylzirconium or (η5-1,5-dimethylindenyl)dimethylzirconium
Metallocene catalyst of Formula VI.  (Formula VI)	bis(n-butylcylcopentadienyl)zirconium dimethyl

Table 1B – Activator

Activator	Chemical name
Spray dried methyl aluminoxane (SDMAO)	Spray dried methyl aluminoxane (SDMAO)

1. Bimodal catalyst systems

[0080] Bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl is the compound of Formula (III).

[0073] CA-300: a continuity additive available from Univation Technologies, LLC. Added to gas phase polymerization reactor to decrease static buildup.

[0074] 1-hexene Comonomer: $H_2C=C(H)(CH_2)_3CH_3$. Comonomer co-polymerized with ethylene in the gas phase polymerization reactor.

[0075] Ethylene ("C_2"): $CH_2=CH_2$. Monomer polymerized in the gas phase polymerization reactor. When copolymerized with 1-hexene, makes ethylene/1-hexene copolymer.

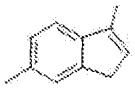
[0076] ICA: a mixture consisting essentially of at least 95%, alternatively at least 98% of 2-methylbutane (isopentane) and minor constituents that at least include pentane

($CH_3(CH_2)_3CH_3$). May be added to the gas phase polymerization reactor to enable condensing mode operation thereof.

[0077] Molecular hydrogen gas: H_2. May be added to the gas phase polymerization reactor to alter molecular weight of the polyethylene produced therein.

[0078] Mineral oil: Sonneborn HYDROBRITE 380 PO White. May be used as a carrier liquid for feeding catalyst into a gas phase polymerization reactor.

[0079] Preparation 1:

[0080] Synthesis of 3,6-dimethyl-1*H*-indene, of the formula . In a glove box, a 250-mL two-neck container fitted with a thermometer (side neck) and a solids addition funnel, was charged with tetrahydrofuran (25 mL) and methylmagnesium bromide (2 equivalents, 18.24 mL, 54.72 mmol). The contents of the container were cooled in a freezer set at -35 °C for 40 minutes; when removed from the freezer, the contents of the container were measured to be -12 °C. While stirring, indanone [5-Methyl-2,3-dihydro-1H-inden-1-one (catalog #HC-2282)] (1 equivalent, 4.000 g, 27.36 mmol) was added to the container as a solid in small portions and the temperature increased due to exothermic reaction; additions were controlled to keep the temperature at or below room temperature. Once the addition was complete, the funnel was removed, and the container was sealed (SUBA). The sealed container was moved to a fume hood (with the contents already at room temperature) and put under a nitrogen purge, then stirred for 3 hours. The nitrogen purge was removed, diethyl ether (25 mL) was added to the container to replace evaporated solvent, and then the reaction was cooled using an acetone/ice bath.

[0081] A HCl (15% volume) solution (9 equivalents, 50.67 mL, 246.3 mmol) was added to the contents of the container very slowly using an addition funnel, the temperature was maintained below 10 °C. Then, the contents of the container were warmed up slowly for approximately 12 hours (with the bath in place). Then, the contents of the container were transferred to a separatory funnel and the phases were isolated. The aqueous phase was washed with diethyl ether (3 times 25 mL). The combined organic phases were then washed with sodium bicarbonate (50 mL, saturated aqueous solution), water (50 mL), and brine (50 mL). The organic phase was

dried over magnesium sulfate, filtered and the solvent removed by rotary evaporator. The resulting dark oil, confirmed as product by NMR, was dissolved in pentane (25 mL), then filtered through a short silica plug (pre-wetted with pentane) that was capped with sodium sulfate. Additional pentane (25-35 mL) was used to flush the plug, then were combined with the first. The solution was dried by rotary evaporator resulting in 2.87 g (74% yield) of 3,6-dimethyl-1H-indene that was confirmed as product by NMR. ^{1}H NMR (C_6D_6): δ 7.18 (d, 1H), 7.09 (s, 1H), 7.08 (d, 1H), 5.93 (m, 1H), 3.07 (m, 2H), 2.27 (s, 3H), 2.01 (q, 3H).

[0082] Preparation 2

[0083] Synthesis of (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl, which is Formula (V). In a glovebox under an anhydrous inert gas atmosphere (anhydrous nitrogen or argon gas), 3,6-dimethyl-1H-indene (1.000g, 6.94 moles) in dimethoxyethane (10 mL) was added to a 120 mL (4-ounce (oz)) container, which was then capped, and the contents of the container were chilled to -35 °C. *n*-butyllithium (1.6M hexanes, 4.3 mL, 0.0069 mole) was added to the container and the contents were stirred for approximately 3 hours while heat was removed to maintain the contents of the container near -35 °C. Reaction progress was monitored by dissolving a small aliquot in d8-THF for ^{1}H NMR analysis; when the reaction was complete, solid cyclopentadienyl zirconium trichloride ($CpZrCl_3$) (1.821 g) was added in portions to the contents of the container while stirring. Reaction progress was monitored by dissolving a small aliquot in d8-THF for ^{1}H NMR analysis; the reaction was complete after approximately 3 hours and the contents of the container were stirred for approximately 12 more hours. Then, methylmagnesium bromide (3.0M in ether, 4.6 mL) was added to the contents of the container, after the addition the contents of the container were stirred for approximately 12 hours. Then, solvent was removed in vacuo and the product was extracted into hexane (40 mL) and filtered through diatomaceous earth, washed with additional hexane (30 mL) and then dried in vacuo to provide the cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl. (Cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Forumla V) was confirmed by proton nuclear magnetic

resonance spectroscopy (^{1}H NMR) analysis. ^{1}H NMR (C_6D_6): δ 7.26 (d, 1H), 6.92 (d, 1H), 6.83 (dd, 1H), 5.69 (d, 1H), 5.65 (m, 1H), 5.64 (s, 5H), 2.18 (s, 3H), 2.16 (s, 3H), -0.34 (s, 3H), -0.62 (s, 3H).

[0084] Due to the rules of IUPAC nomenclature, it is believed that the dimethyl numbering in the molecule 3,6-dimethyl-1*H*-indene becomes, after deprotonation thereof, becomes in the conjugate anion 1,5-dimethylindenyl.

[0085] Preparation 3

[0086] Preparation of Bimodal Catalyst System 1 (AFS-BMCS1). Slurry 70.3 parts by weight of treated fumed silica (CABOSIL TS-610) in 1000 parts by weight of toluene, followed by adding 171 parts by weight of a 30 wt% solution of methylaluminoxane (MAO) in toluene, 3.54 parts by weight of the bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl (Formula III) and 0.229 parts by weight of cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl (Formula V) of Preparation 2 to give a mixture. Using a spray dryer set at 160° C. and with an outlet temperature at 70° to 80° C, introduce the mixture into an atomizing device of the spray dryer to produce droplets of the mixture, which are then contacted with a hot nitrogen gas stream to evaporate the liquid from the mixture to give a powder. Separate the powder from the gas mixture in a cyclone separator and discharge the separated powder into a container to give the Bimodal Catalyst System 1 ("BMCS1") as a fine powder. Slurry the resultant powder form of BMCS1 to give an activator formulation slurry form of BMCS1 ("AFS-BMCS1") of 22 wt% solids in 10 wt% isoparaffin fluid and 68 wt% mineral oil.

[0087] Preparation 4

[0088] Preparation of Trim Catalyst Solution 1 ("TCS1") comprising a trim solution of cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl (Formula V) in n-hexane and isopentane. Charge (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V) and n-hexane into a first cylinder. Charge the resulting solution of (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl solution in hexane from the first cylinder into a 106 liter (L; 28 gallons) second cylinder. The second cylinder contained 310 grams of 1.07 wt %

(cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V). Added 7.98 kg (17.6 pounds) of high purity isopentane to the 106 L cylinder to yield the Trim Catalyst Solution 1 of 0.04 wt % (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V) in n-hexane and isopentane.

[0089] Preparation 5

[0090] Preparation of Trim Catalyst Solution 2 ("TCS2"). Weigh 4.03 grams of solid powder bis(2,4-di-*t*-butyl-6-isopropylamino phenoxy imine) zirconium dibenzyl (Formula I) into a first beaker. Add 568 grams of hexane to solid powder and mix. Charge the resulting solution into a first cylinder. Transfer first cylinder into a 106 liter (L; 28 gallons) second cylinder. The second cylinder contained 572.03 grams of the mixture. Added 9.4 kg (20.8 pounds) of high purity isopentane to the 106 L cylinder to yield the Trim Catalyst Solution 2.

[0091] Polymerization Procedure

[0092] Inventive Examples IE1, IE2 and comparative sample 1 (CS1) described below, were prepared by copolymerizing ethylene and 1-hexene using the Activator Formulation Slurry form of Bimodal Catalyst System 1 (AFS-BMCS1) and a controlled relative amount of the Trim Catalyst Solution 1 (TCS1) or Trim Catalyst Solution 2 (TCS2) in a fluidized bed-gas phase polymerization (FB-GPP) reactor having a distribution grid to make an embodiment of the trimodal poly(ethylene-*co*-1-alkene) copolymer that is a trimodal poly(ethylene-*co*-1-hexene) copolymer. The FB-GPP reactor had a 0.35 meter (m) internal diameter and 2.3 m bed height and a fluidized bed composed of polymer granules. Fluidization gas flowed through a recycle gas loop comprising sequentially a recycle gas compressor and a shell-and-tube heat exchanger having a water side and a gas side. The fluidization gas flowed through the compressor, then the water side of the shell-and-tube heat exchanger, then into the FB-GPP reactor below the distribution grid. Fluidization gas velocity was about 0.55 to 0.61 meter per second (m/s, 1.8 to 2.0 feet per second). The fluidization gas then exited the FB-GPP reactor through a nozzle in the top of the reactor and was recirculated continuously through the recycle gas loop.

[0093] A constant fluidized bed temperature was maintained by continuously adjusting the temperature of the water on the shell side of the shell-and-tube heat exchanger. Introduced feed streams of ethylene, nitrogen, and hydrogen together with the 1-hexene comonomer into the recycle gas line. The FB-GPP reactor was operated at a total pressure of about 2420 kPa gauge, and vented reactor gases were flared to control the total pressure. Individual flow rates of ethylene, nitrogen, hydrogen and the 1-hexene were adjusted to maintain their respective gas composition targets. Ethylene partial pressure was set to 1.52 megapascal (MPa, 220 pounds per square inch (psi)), and the C_6/C_2 molar ratio and the H_2/C_2 molar ratio were set as specified.

[0094] Average copolymer residence time was from 1.9 to 4.1 hours. Concentrations of all gasses were measured using an on-line gas chromatograph. The fluidized bed was maintained at constant height by withdrawing a portion of the bed at a rate equal to the rate of formation of particulate product trimodal ethylene/hexene copolymer. Product was removed semi-continuously via a series of valves into a fixed volume chamber. A nitrogen purge removed a significant portion of entrained and dissolved hydrocarbons in the fixed volume chamber. After purging, the product was discharged from the fixed volume chamber into a fiber pack for collection. The product was further treated with a small stream of humidified nitrogen to deactivate any trace quantities of residual catalyst and cocatalyst. The ratio feed of trim catalyst solution 1 (TCS1) or trim catalyst solution 2 (TCS2) was set to the feed of the bimodal catalyst system AFS-BMCS1 to adjust the HLMI (I_{21}) of the produced trimodal ethylene/hexene copolymer in the reactor to achieve the desired target. The catalyst feeds were set at rates sufficient to maintain a production rate of about 12 to about 20 kg/hour (about 26 to about 44 lbs/hr) of the trimodal ethylene/hexene copolymer.

[0095] The polymerization conditions and process results are described in Table 2 below.

[0096] Table 2: Polymerization Conditions of IE1-2 and CS1.

Polymerization Conditions	CS1	IE1	IE2
Bed Temperature (° C.)	95	90	90
Reactor Pressure (kPa)	2420	2420	2420
Ethylene ("C_2") Partial Pressure (kPa)	1517	1517	1517
H_2/C_2 Molar Ratio	0.0039	0.0040	0.0040
1-hexene/ethylene ("C_6/C_2") Molar Ratio	0.0071	0.0064	0.0059
Induced Condensing Agent 1-methylbutane (mol%)	11.1	11.9	12.0
Superficial Gas Velocity (m/sec)	0.61	0.55	0.55
Bimodal Catalyst System	AFS-BMCS1	AFS-BMCS1	AFS-BMCS1
Trim Catalyst Solution	TCS1	TCS2	TCS2
TCS1 / AFS-BMCS1 mass flow ratio	3.5	0	0
TCS2 / AFS-BMCS1 mass flow ratio	0	9.7	8.5
CA-300 Continuity Additive (ppm)	42	63	54
Catalyst Zr conc. (wt%)	0.43	0.45	0.45
Catalyst Al conc. (wt%)	18.85	19.80	19.80
Starting seedbed = granular HDPE resin	Preloaded	Preloaded	Preloaded
Fluidized Bed Weight (kg)	50	39	39
Copolymer Production Rate (kg/hour)	12	14	20
Copolymer Residence Time (hour)	4.1	2.9	2.0
Copolymer Fluid Bulk Density, (kg/m^3)	268	263	271
I21 (g/10 min)	8.5	8.5	8.2
I5 (g/10 min)	0.31	0.40	0.40
I21/I5	27.9	21.0	20.7
Density (g/cm^3)	0.9492	0.9489	0.9497

[00105] Inventive Examples 1 to 2 (IE1, IE2): produced trimodal ethylene/-hexene copolymer and were synthesized using the Polymerization Procedure described above and Activator Formulation Slurry form of Bimodal Catalyst System 1 (AFS-BMCS1) and Trim Catalyst Solution 2 (TCS2).

[00106] Comparative Sample 1 (CS1) produced a trimodal ethylene/hexene copolymer and was synthesized using the Polymerization Procedure described above, and Activator Formulation Slurry form of Bimodal Catalyst System 1 (AFS-BMCS1) and Trim Catalyst Solution 1 (TCS1).

[00107] Table 3 -Reactor conditions and properties for trimodal resin are provided in below.

[00108] Table 3 – Reactor conditions and polymer properties

sample	Cat	T (C)	H2/C2	C6/C2	ICA %	Res Time (hr)	Trim /cat	d	I5/I21	Mn	Mw	Mz	Mw/Mn	Split (% HMW)	Mp LMW	Mp HMW	Spread	BBF	Vinyl	Olig
CS1	Formill/FormV Trim: FormV	95	0.0042	0.0071	11.1	4.1	3.5	0.9492	0.31/ 8.5	9,030	299,702	2,654,793	33.19	54.86	12,023	245,471	233,448	1.81	0.080	1185
IE1	Formill/FormV Trim: FI-A	90	0.0040	0.0064	11.9	2.9	9.7	0.9489	0.40/ 8.5	15,141	264,001	2,245,297	17.44	56.12	18,621	204,174	185,553	1.35	0.494	204
IE2	Formill/FormV Trim: FI-A	90	0.0040	0.0060	11.9	2.0	9.6	0.9496	0.41/ 8.6	15,163	263,211	2,215,588	17.36	56.72	18,621	204,174	285,553	1.26	0.490	Nm

Olig – oligomer C_6-C_{16}, ppm

[00109] As detailed in Table 3, the resultant trimodal ethylene/hexene copolymer resins of IE1 and IE2 provide for the use of an unsupported trim catalyst solution of a phenoxy imine olefin polymerization catalyst in hexane. As detailed in Table 3, the resultant trimodal resins of IE1 and IE2 have one, some, or all, of the following properties:

(i) density from 0.940 g/cc to 0.950 g/cc; and/or

(ii) a molecular mass dispersity (M_w/M_n) from 10.0 to 250; and/or

(iii) a weight-average molecular weight (M_W) from 200,000 g/mol to 275,000 g/mol; and/or

(iv) a number-average molecular weight (M_n) from 10,000 g/mol to 20,000 g/mol; and/or

(v)a z-average molecular weight (M_Z) from 2,000,000 g/mol to 2,500,000 g/mol; and/or

(iv) a butyl branch frequency from 1.1 to 1.7 butyl branches per 1000 carbon; and/or

(vii) a vinyl content from 0.2 to 0.6 to 1000 carbon; and/or

(viii) a high molecular weight split greater than 55%; and/or

(ix) an oligomer content less than 500 ppm, and

(x) combinations thereof.

[00110] The resultant trimodal ethylene/hexene copolymer resins of IE1 and IE2 further provide an improved (i.e., lower) molecular weight than resins made from comparative trimodal systems. For instance, each of IE1-2 provides a resin having a molecular weight in the range from 264,001 Daltons to 263,211 Daltons, which may be desirable for certain applications.

[00111] As detailed in Table 3, IE1, IE2 each provide a trimodal resin having less oligomer compared to the comparative sample (CS1). Still further, as detailed in Table 3, IE1-2 each provide a trimodal resin having higher vinyl end group content per 1000 C as compared to other (CS1) catalyst resin.

[00112] As demonstrated by IE1-2, the high molecular weight (HMW) tail of the resultant resin may be adjusted by process conditions, namely, residence time effect. Specifically, lower residence time (RT), as evidenced by the polymerizing conditions of IE2 relative to IE1, results in a corresponding decrease HMW tail and M_W.

[00113] It is specifically intended that the present disclosure is not limited to the embodiments and illustrations contained herein but include modified forms of those embodiments including portions of the embodiments and combination of elements of different embodiments as come within the scope of the following claims.

CLAIMS

1. A catalyst system, comprising:

a bimodal catalyst (BMC) spray-dried to a support;

a trim catalyst comprising a phenoxy imine catalyst selected from a group consisting of

(i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl and

(ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride; and

at least one spray-dried methylaluminoxane activator.

2. The catalyst system of claim 1, wherein the BMC comprises

(i) a non-metallocene catalyst, and

(ii) a metallocene catalyst.

3. The catalyst system of claim 2 wherein the non-metallocene catalyst is bis(2-pentamethylphenylamido)ethyl)-amine zirconium dibenzyl).

4. The catalyst system of claim 3 wherein the metallocene catalyst is selected from the group consisting of methylcyclopentadienyl (1, 3-dimethyl-4, 5, 6, 7-tetrahydroindenyl) zirconium dimethyl, η5-cyclopentadienyl)(η5-1,5-dimethylindenyl)dimethylzirconium bis(N-butylcyclopentadienyl) zirconium dimethyl, and combinations thereof.

5. The catalyst system of any of claims 1-4 having a ratio of trim catalyst to BMC from 0.1 to 20.

6. The catalyst system of claim 1, wherein the trim catalyst is present in an amount from 0.01 wt% to 1.5 wt% in a hexane solvent based on total weight of the trim catalyst and the solvent.

7. The catalyst system of any of claims 1-6, wherein the trim catalyst is unsupported.

8. The catalyst system of any of claims 1-7, wherein the BMC is spray-dried to a fused silica support.

9. A process comprising:

polymerizing ethylene with one or more α-olefins, under polymerization conditions, with a catalyst system comprising

a BMC spray-dried to a support,

a trim catalyst comprising a phenoxy imine catalyst selected from a group consisting of

(i) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl and

(ii) bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dichloride, and

at least one spray-dried methylaluminoxane activator; and

forming a trimodal ethylene/α-olefin terpolymer.

10. The process of claim 9, wherein the polymerization conditions comprise a variable selected from the group consisting of

(i) a reaction temperature from 75°C to 110°C,

(ii) a molar ratio of the hydrogen gas to the ethylene from 0.0035 to 0.0045,

(iii) a molar ratio of the α-olefin to the ethylene from 0.0040 to 0.0070,

(iv) a reactor residence time from 2.0 to 2.9 hours, and

(v) combinations thereof.

11. The process of any of claims 9-10 wherein the α-olefin is selected from a group consisting of (i)1-butene, (ii)1-hexene (iii) 1-octene, and (iv) combinations thereof.

12. The process of any of claims 9-11 comprising

forming a trimodal ethylene/olefin terpolymer having a property selected from the group consisting of

(i) density from 0.930 g/cc to 0.960 g/cc,

(ii) a molecular mass dispersity (M_w/M_n) from 10.0 to 25.0,

(iii) a weight-average molecular weight (M_W) from 200,000 g/mol to 275,000 g/mol,

(iv) a number-average molecular weight (M_n) from 10,000 g/mol to 20,000 g/mol,

(v)a z-average molecular weight (M_z) from 2,000,000 g/mol to 2,500,000 g/mol,

(iv) a butyl branch frequency from 1.1 to 1.7 butyl branches per 1000 carbon,

(vii) a vinyl content from 0.20 to 0.60 per 1000 carbon atom,

(viii) a high molecular weight split greater than 55%,

(ix) an oligomer content less than 500 ppm, and

(x) combinations thereof.

13. The process of any of claims 9-12 wherein the olefin is hexene and the process comprises

forming a trimodal ethylene/hexene copolymer.