

POLYETHYLENE CATALYST SYSTEM AND PROCESS

BACKGROUND

[0001] Gas-phase single reactor bimodal technologies provide for the synthesis of olefin terpolymers (and ethylene/ α -olefin terpolymers in particular) polymerized with a high molecular weight component and a low molecular weight component. However, utilization of a single polymerization reactor limits the comonomer distribution across the high molecular weight component ("HMW") and the low molecular weight component ("LMW") of the bimodal terpolymer. Bimodal polymers with proportionally more comonomer content in the HMW component are known to exhibit an improved balance of various product properties, such as improved balance of slow crack growth resistance (SCGR) and long-term hydrostatic test performance (for pipes); improved balance of environmental stress cracking resistance (ESCR) and swell properties for (blow molded articles); and improved balance of ESCR and processability for wire and cable applications.

[0002] The art recognizes the need for olefin-based polymer (and ethylene/ α -olefin polymers in particular) synthesis performed in a single gas-phase reactor, the ethylene/ α -olefin polymer having improved comonomer distribution across the HMW component and the LMW component. The art further recognizes the need for improved catalyst lifetime as a function of residence time.

SUMMARY

[0003] The present disclosure provides a catalyst system. In an embodiment, the catalyst system includes (A) a first catalyst and (B) 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 (C) at least one spray-dried methylaluminoxane activator.

[0004] The present disclosure provides a process. In an embodiment, the process includes polymerizing ethylene with one or more olefins, under polymerization conditions, with a catalyst system. The catalyst system includes (A) a first catalyst and (B) 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 (C) at least one spray-dried methylaluminoxane activator. The process includes forming a bimodal ethylene/olefin terpolymer composition.

DEFINITIONS

[0005] 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.

[0006] 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.

[0007] 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.).

[0008] 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.

[0009] “Bimodal,” as used herein, refers to two, and only two, modalities, or modes.

[0010] A “bimodal catalyst system” 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. 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, one catalyst, i.e., the non-metallocene catalyst contained within the bimodal catalyst system may be disposed on a support material, to which the trim catalyst is introduced in the reactor.

[0011] A “bimodal polymer composition” (e.g., an ethylene/olefin terpolymer composition) is a composition composed of (i) high molecular weight component (“HMW”), and (iii) low molecular weight component (LMW”), wherein the high molecular weight component consists of a first group of polymer macromolecules made by a first catalyst, and the low molecular weight component consists of a second group of polymer macromolecules made by a second catalyst, wherein at least one of the following differences are present: (a) the catalysts are different in catalytic metal and/or ligand composition; (b) the polymerization reaction making the higher molecular weight component is done at a different time than the polymerization reaction making the lower molecular weight component; (c) at least one of the first set of molecular weight-effective polymerization process conditions is different than one of the second set of molecular weight-effective polymerization process conditions. Bimodal polymer compositions are in-reactor blends. The bimodal polymer composition may be characterized by two peaks separated by a distinguishable local minimum therebetween in a plot of $dW/d\log(MW)$ on the y-axis versus $\log(MW)$ on the x-axis to give a Gel Permeation Chromatograph (GPC) chromatogram, wherein $\log(MW)$ and $dW/d\log(MW)$ are as defined herein and are measured by Gel Permeation Chromatograph (GPC) Test Method described herein.

[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" (interchangeably referred to as "polyethylene") 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 of (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. 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 cyclopentadienyl 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 (C₁ – C₄) 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 two 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. 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 copolymer" and "propylene/ α -olefin copolymer" 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 may optionally be used in combination with a non-metallocene catalyst and/or a metallocene catalyst to create the resultant bimodal 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 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 ($M_w/M_n/M_z$), and any combination thereof.

[0026] A “unimodal catalyst system” is a catalyst system that contains one catalyst for catalyzing a polymerization process (e.g., olefin polymerization) and producing a unimodal polymer composition. As described herein the catalyst of the unimodal catalyst system may be a trim catalyst that is introduced to an activator in the gas phase polymerization reactor.

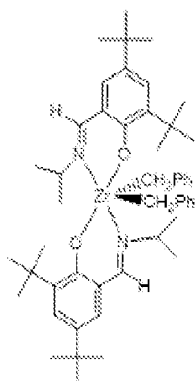
DETAILED DESCRIPTION

[0027] The present disclosure provides a catalyst system. In an embodiment, the catalyst system includes (A) a first catalyst and (B) 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 (C) at least one spray-dried methylaluminoxane activator.

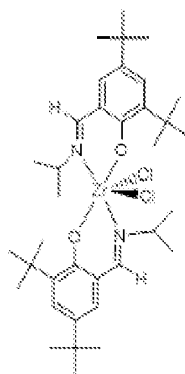
[0028] The catalyst system includes the first catalyst. The first catalyst is a non-metallocene catalyst, a metallocene catalyst, and combinations thereof. A “non-metallocene catalyst,” is a catalyst that is not a metallocene catalyst. In other words, a non-metallocene catalyst is a catalyst that does not include a cyclopentadienyl ligand—metal complex. A nonlimiting example for the non-metallocene catalyst includes bis (2-pentamethylphenylamido)ethyl)-amine zirconium dibenzyl).

[0029] Nonlimiting examples for the metallocene catalyst include methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl, 5-cyclopentadienyl)(η 5-1,5-dimethylindenyl)dimethylzirconium or (η 5-1,5-dimethylindenyl)dimethylzirconium, and bis(n-butylcyclopentadienyl)zirconium dimethyl.

[0030] The catalyst system includes the trim catalyst. The trim catalyst in the inventive examples 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 below:



(Formula I)



(Formula II).

[0031] 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.

[0032] 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-(CF₃)₂phenyl)borate, Triphenylcarbenium tetrakis(3,5-(CF₃)₂phenyl)borate, dimethylanilinium tetrakis(perfluoronaphthyl)borate, Triphenylcarbenium tetrakis(perfluoronaphthyl)borate, dimethylanilinium tetrakis(pentafluorophenyl)aluminate, triphenylcarbenium tetrakis(pentafluorophenyl)aluminate, Dimethylanilinium tetrakis(perfluoronaphthyl)aluminate, triphenylcarbenium tetrakis(perfluoronaphthyl)aluminate, a tris(perfluorophenyl)boron, a

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

[0033] In an embodiment, the activator is an aluminoxane. An "aluminoxane" is an oligomeric aluminum compound 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.

[0034] 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 ("TiBAI"), tri-n-hexylaluminum, tri-n-octylaluminum, tripropylaluminum, tributylaluminum, and combinations thereof.

[0035] 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.

[0036] 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.

[0037] A nonlimiting example of a support is fumed silica available under the trade name Cabosil™ TS- 610, or other TS- or TG-series support, 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.

[0038] In an embodiment, the support material has a surface area in the range from 10 to 700 m²/g, pore volume in the range from 0.1 to 4.0 g/cm³ and an average particle size in the range from 5 to 500 microns. More preferably, the surface area of the support material is in the range from 50 to 500 m²/g, pore volume from 0.5 to 3.5 g/cm³ and average particle size of from 10 to 200 microns. Most preferably the surface area of the support material is in the range from 100 to 400 m²/g, pore volume from 0.8 to 3.0 g/cm³ and average particle size is from 5 to 100 microns. The average pore size of the support material typically has pore size in the range of from 10 to 1000 Angstroms (Å) or from 50 to 500Å, or from 75 to 350Å.

[0039] The solid support may be an uncalcined material or a calcined material prior to being contacted with the activator. The solid support material may be a hydrophobic fumed silica (e.g., a fumed silica treated with dimethyldichlorosilane). The activator spray-dried to the support may be in the form of a powdery, free-flowing particulate solid.

[0040] In an embodiment, the activator is methylaluminoxane spray-dried to a hydrophobic fumed silica support.

[0041] In an embodiment, the catalyst system includes the first catalyst, the trim catalyst (FI-A and/or FI-B) and also includes at least one methylaluminoxane activator spray-dried on a fumed silica support.

[0042] In an embodiment, the catalyst system includes the (A) first catalyst that is a non-metallocene catalyst, (B) the trim catalyst (FI-A and/or FI-B), and (C) methylaluminoxane activator spray-dried on a fumed silica support. Nonlimiting examples for the non-metallocene catalyst include bis(2-pentamethylphenylamido)ethyl)-amine zirconium dibenzyl).

[0043] In an embodiment, the catalyst system includes (A) the first catalyst that is a metallocene catalyst, (B) the trim catalyst (FI-A and/or FI-B), and (C) methylaluminoxane activator spray-dried on a fumed silica support. Nonlimiting examples for the metallocene catalyst include metallocene Y-123, H-15 and B.

[0044] The first catalyst is spray-dried to a support. The support may be any support material as previously disclosed herein. In an embodiment, the support for the non-metallocene/metallocene catalyst is selected from 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.

[0045] In an embodiment, the support for first catalyst is fumed silica.

[0046] In an embodiment trim catalyst (the phenoxy imine catalyst) is dissolved in an alkane solvent (such as hexane for example) and/or mineral oil. The phenoxy imine catalyst is present from 0.5 wt% to 4.0 wt%, or from 0.5 wt% to 1.5 wt%, or 1.0 wt% wherein weight percent is based on the total weight of the phenoxy imine catalyst and solvent. The trim catalyst/solvent is injected into the polymerization reactor before, during, or after the introduction of the first catalyst and/or activator into the polymerization reactor.

[0047] In an embodiment, the phenoxy imine catalyst is unsupported.

[0048] In an embodiment, the trim catalyst is supported and is spray-dried to a fumed silica support. The supported trim catalyst is introduced into the polymerization reactor before, during, or after the introduction of the first catalyst and/or activator into the polymerization reactor.

Process

[0049] The present disclosure provides a process. In an embodiment, the process includes polymerizing ethylene with one or more olefins, under polymerization conditions, with a catalyst system composed of (A) the first catalyst, (B) the trim catalyst and (C) the activator. The first catalyst is a non-metallocene catalyst or a metallocene catalyst as disclosed above. 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 methyl aluminoxane activator. The process includes forming a bimodal ethylene/olefin terpolymer composition.

[0050] 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”) reactor or a composition or property of a polymer 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 H₂ and/or O₂, molar ratio of feed gases versus reactants, absence or concentration of interfering materials (e.g., H₂O), 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 those being described or changed by the process may be kept constant.

[0051] 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 polymer composition. For example, the FB-GPP reactor/method may be as described in US 3,709,853; US 4,003,712; US 4,011,382; 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.

[0052] 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

("C₂"), hydrogen ("H₂") and olefin (such as 1-hexene ("C₆")) are controlled to maintain a fixed comonomer to ethylene monomer gas molar ratio (C₆/C₂) equal to a described value, a constant hydrogen to ethylene gas molar ratio ("H₂/C₂") equal to a described value, and a constant ethylene ("C₂") partial pressure equal to a described value.

[0053] 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 1861 kilopascals (kPa) to 2413 kPa (270 pounds per square inch-gauge (psig) to 350 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 polymer composition, which production rate may be from 10 kg/hr to 100 kg/hr (pilot plant) or from 1,000 kg/hr to 50,000 kg/hr (industrial scale production). The product polymer composition is removed semi-continuously via a series of valves into a fixed volume chamber, wherein the removed polymer composition is purged to remove entrained hydrocarbons and treated with a stream of humidified nitrogen (N₂) gas to deactivate any trace quantities of residual catalyst.

[0054] Start-up or restart of the GPP reactor may be illustrated with a fluidized bed, GPP reactor. The start-up of a recommissioned FB-GPP reactor (cold start) or restart of a transitioning FB-GPP reactor (warm start) includes a time period that is prior to reaching steady-state polymerization conditions of step (a). Start-up or restart may include the use of a polymer seedbed preloaded or loaded, respectively, into the fluidized bed reactor. The polymer seedbed may be composed of powder of a polyethylene such as a polyethylene homopolymer or previously made batch of the bimodal polymer composition.

[0055] 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.

[0056] 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.

[0057] In an embodiment, the process includes 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 catalyst system, once its catalysts are activated, may be fed into the GPP reactor as a dry powder, alternatively as a slurry in a non-polar, aprotic (hydrocarbon) solvent. In option (c) the 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 non-metallocene catalyst (if present) and trim catalyst *in situ*.

[0058] The process includes polymerizing, or otherwise contacting, ethylene with one or more olefins, under polymerization conditions, with the 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.

[0059] 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.

[0060] The process includes forming a bimodal ethylene/olefin terpolymer composition. Nonlimiting examples of bimodal ethylene/olefin terpolymers include bimodal 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, vinylbenzocyclobutene, styrene, 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 an 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 copolymer. "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.

[0061] The bimodal ethylene/olefin terpolymer composition can include from 50 wt% to 99 wt%, or 50 wt% to 95 wt % units derived from ethylene and from 50 wt% to 1 wt%, or from 50 wt% to 5 wt% units derived from one or more olefins, or from 60 wt % to 90 wt%, of

units derived from ethylene and 40 wt% to 10 wt% units derived from one or more olefins, or from 70 wt% to 85 wt% units derived from ethylene and from 30 wt% to 15 wt% units derived from one or more olefins, wherein weight percent is based on the total weight of the terpolymer.

[0062] In an embodiment, the polymerization conditions include contacting a catalyst system with ethylene and a C₄-C₈ α -olefin comonomer, or hexene, under polymerization conditions the catalyst system including (A) a first catalyst that is a non-metallocene catalyst, (B) a trim catalyst and (C) an activator, and controlling, providing, or otherwise adjusting one, some, or all of the following variables:

- (i) a reaction temperature from 75°C to 105°C, or from 90°C to less than 100°C, and/or
- (ii) a molar ratio of the hydrogen gas to the ethylene from 0.0010 to 0.0070, or from 0.0020 to 0.0060, and/or,
- (iii) a molar ratio of the olefin to the ethylene from 0.0050 to 0.0400, or from 0.0055 to 0.0200, and/or
- (iv) a reactor residence time from 1.0 hours to 4.5 hours, or from 1.0 hours to 3.0 hours or from 2.0 to 3.0 hours, and

the process includes forming a bimodal ethylene/C₄-C₈ α -olefin copolymer (or a bimodal ethylene/hexene copolymer) having one, some, or all of the following properties:

- (i) a HMW split greater than 50%;
- (ii) an oligomer content less than 100 ppm;
- (iii) a density from 0.935 to 0.970 g/cm³, or from 0.935 g/cm³ to 0.950 g/cm³; and/or
- (iv) a molecular mass dispersity (M_w/M_n) from 5.0 to 20.0, or from 5.5 to 18.0; and/or,
- (v) a weight-average molecular weight (M_w) from 100,000 g/mol to 400,000 g/mol, or from 200,000 g/mol to 350,000 g/mol; and/or
- (vi) a number-average molecular weight (M_n) from 10,000 g/mol to 30,000 g/mol, or from 15,000 g/mol to 25,000 g/mol; and/or
- (vii) a z-average molecular weight (M_z) from 1,500,000 g/mol to 4,000,000 g/mol, or from 2,000,000 g/mol to 3,000,000 g/mol; and/or

(viii) a butyl branch frequency from 1.0 to 7.0 butyl branches per 1000 carbon atom, or from 1.0 to 1.5 butyl branches per 1000 carbon atom; and/or

(ix) a vinyl content from 0.5 per 1000 carbon atom to less than 1.0 per 1000 carbon atom, or from 0.5 per 1000 carbon atom to 0.8 per 1000 carbon atom.

[0063] As mentioned, surprisingly, the phenoxy imine olefin polymerization catalyst is particularly well adapted to help to provide bimodal polymers and particularly bimodal ethylene/olefin copolymer via a polymerization process in a gas-phase polymerization reactor independently or in combination with other polymerization catalysts. For instance, the resultant bimodal ethylene/olefin copolymer can have an improved, i.e., higher, Mw/Mn as detailed herein, as compared to polymers made with other (non-inventive) polymerization catalysts at similar polymerization conditions. An increased Mw/Mn is desirable in some applications. Similarly, the resultant bimodal ethylene/olefin copolymer can have at least a high molecular weight polyethylene component and a low molecular weight polyethylene component, as detailed herein. Having a high molecular weight polyethylene component and a low molecular weight polyethylene component is desirable in some applications.

[0064] In an embodiment, the polymerization conditions include a gas-phase polymerization reactor and the process includes contacting a catalyst system with ethylene and a C₄-C₈ α -olefin comonomer, or hexene, under polymerization conditions, the catalyst system including (A) a first catalyst that is a non-metallocene catalyst, (B) a trim catalyst FI-A or FI-B and (C) an activator, and controlling, providing, or otherwise adjusting one, some, or all of the following variables:

- (i) a reaction temperature from 75°C to 105°C, or from 90°C to 105°C, and/or
- (ii) a molar ratio of the hydrogen gas to the ethylene from 0.0010 to 0.0070, or from 0.0020 to 0.0060, or from 0.0020 to 0.0050 and/or,
- (iii) a molar ratio of the hexene to the ethylene from 0.0005 to 0.0400, or from 0.0050 to 0.0300, and/or
- (iv) a reactor residence time from 1.5 hours to 4.5 hours, or from 1.5 hours to 3.0 hours, or from 2.0 to 3.0 hours, and

the process includes forming a bimodal ethylene/C₄-C₈ α -olefin copolymer (or a bimodal ethylene/hexene copolymer) having one, some or all of the following properties:

(i) a HMW split greater than 50%, or from 51% to 75%, or from 51%, to 65%, or from 51% to 60%; and/or

(ii) an oligomer content less than 100ppm, or 0 ppm, or from greater than 0 ppm to less than 90 ppm, or from 1 ppm to 50 ppm, or from 2 ppm to 25 ppm, or from 2 ppm to 10 ppm; and/or

(iii) a density from 0.935 to 0.950 g/cm³, or from 0.948 g/cm³ to 0.949 g/cm³; and/or

(iv) a molecular mass dispersity (M_w/M_n) from 5.0 to 20.0, or from 10.0 to 18.0 or from 12.5 to 16.0; and or,

(v) a weight-average molecular weight (M_w) from 200,000 g/mol to 325,000 g/mol, or from 259,378 g/mol to 307,753 g/mol; and/or

(vi) a number-average molecular weight (M_n) from 15,000 g/mol to 25,000 g/mol, or from 19,751 g/mol to 20,278 g/mol; and/or

(vii) a z-average molecular weight (M_z) from 2,000,000 g/mol to 3,000,000 g/mol, or from 2,354,495 g/mol to 2,909,311 g/mol; and/or

(viii) a butyl branch frequency from 1.0 to 1.5 butyl branches per 1000 carbon atom, or from 1.29 to 1.35 butyl branches per 1000 carbon atom; and/or

(ix) a vinyl content from 0.45 per 1000 carbon atom to 0.7 per 1000 carbon atom or from 0.6 per 1000 carbon atom to 0.7 per 1000 carbon.

[0065] The ethylene/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.

TEST METHODS

[0066] Butyl Branch Frequency (BBF): Comonomer content is determined using ¹³C 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. [From: Angela: "Manjiri, please review."

[0067] Differential Scanning Calorimetry (DSC). Melt temperature can be determined via Differential Scanning Calorimetry according to ASTM C 3418-08I. For instance, using a scan rate of 10° C./min on a sample of 10 mg and using the second heating cycle.

[0068] 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).

[0069] 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 M_w , M_n , MWD are described in US 2006/0173123 page 24-25, paragraphs [0334] to [0341]. Plot of $dW/d\log(MV)$ on the y-axis versus $\log(MW)$ on the x-axis to give a GPC chromatogram, wherein $\log(MW)$ and $dW/d\log(MV)$ are as defined above.

[0070] 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

[0071] Melt Indices. ("I₂") Test Method: for ethylene-based (co)polymer is measured according to ASTM D1238-13, using conditions of 190° C./2.16 kg. ("I₅") 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 ("I₂₁") 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.).

[0072] ¹H nuclear magnetic resonance (¹H 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=CH₂, wherein R is a carbon atom, or a heteroatom selected from N, O, P, B, S, and Si. Polymer samples for ¹H NMR analysis were prepared by adding 130 mg of sample to 3.25 g of 50/50 by weight tetrachlorethane-d₂/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. ¹H 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, lclprf2.zzl, TD 32768, 100 scans, DS 4, SWH 10,000 Hz, AQ 1.64s, Di 1s, D₁₃ 13s. Vinyl content is reported as the number of vinyl bonds per 1000 carbon atoms (1000C).

[0073] HMW Split. Segment the chromatogram obtained using Gel permeation chromatography (GPC) Test into nine (9) Schulz-Flory molecular weight distributions. Such deconvolution method is described in US 6,534,604. Assign the lowest four MW distributions to the LMW polyethylene component and the five highest MW distributions to the HMW polyethylene component. Determine the respective weight percents (wt%) for each of the LMW and HMW polyethylene components in the inventive bimodal ethylene/olefin terpolymer

composition by using summed values of the weight fractions (W_f) 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.

[0074] 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) is 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; $\mu\text{g/g}$).

[0075] By way of example, and not limitation, examples of the present disclosure will now be described in detail in the following examples.

EXAMPLES

[0076] Table 1 below provides catalysts, used to prepare the comparative samples (CS) and the Inventive Examples (IE).

Table 1A - Catalysts

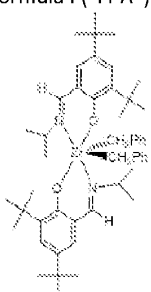
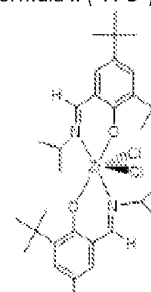
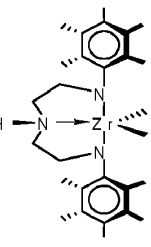
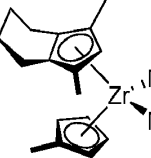
Catalyst	Chemical name
phenoxy imine olefin polymerization catalyst of Formula I ("FI-A")  (Formula I)	Bis(2,4-di-tert-butyl-6 isopropylamino phenoxy imine) zirconium dibenzyl
phenoxy imine olefin polymerization catalyst of Formula II ("FI-B")  (Formula II)	Bis(2,4-di-tert-butyl-6 isopropylamino phenoxy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

Table 1A –Catalysts (continued)

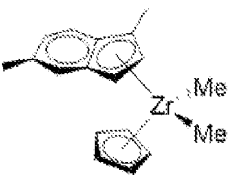
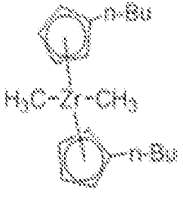
Metallocene catalyst of Formula V  (Formula V)	η^5-cyclopentadienyl)(η^5-1,5-dimethylindenyl)dimethylzirconium or (η^5-1,5-dimethylindenyl)dimethylzirconium
Metallocene catalyst of Formula VI.  (Formula VI)	Bis(n-butylcyclopentadienyl)zirconium dimethyl

Table 1B – Activator

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

[0077] 1. Preparation of Activator Formulation Slurry form of a Catalyst System 1 (“AFS1”).

[0078] A polymerization catalyst system was prepared by slurrying 1.5 kg of treated fumed silica (Cabosil TS-610) in 16.8 kg of toluene, followed by addition of a 10 % solution (11.1 kg) by weight of MAO in toluene and 54.5 g of bis(2-(pentamethylphenylamido)ethyl)amine zirconium dibenzyl (Formula III). The resulting mixture was introduced into an atomizing device, producing droplets that were then contacted with a hot nitrogen gas stream to evaporate the liquid and form a powder. The powder was separated from the gas mixture in a cyclone separator and discharged into a container. The spray drier temperature was set at 160 °C and the outlet temperature at 70-80 °C. The product collected was a fine powder. The resultant powder was then slurried to a final formulation of 16 wt % solids in 10 wt % n-hexane and 74 wt % Sonneborn Hydrobrite® 380 PO White mineral oil to give an activator formulation slurry form of a Catalyst System 1 (“AFS1”).

[0079] 2. Preparation of Activator Formulation Slurry form of a Catalyst System 2 ("AFS2").

[0080] A spray-dried catalyst formulation was prepared from Cabosil™ TS-610, methylaluminoxane, bis(2-(pentamethylphenylamido)ethyl)-amine zirconium dibenzyl (Formula III), and (methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl (Formula IV).

[0081] 3. Preparation of Activator Formulation Slurry form of a Catalyst System 3 ("AFS3").

Spray-dried catalyst formulation of Cabosil™ TS-610, methylaluminoxane, bis(2-(pentamethylphenylamido)ethyl)-amine zirconium dibenzyl (Formula III), and (tetramethylcyclopentadienyl)(n-propylcyclopentadienyl)zirconium dimethyl.

[0082] 4. Preparation of Activator Formulation Slurry form of a Catalyst System 4 ("AFS4").

[0083] 70.3 parts by weight of treated fumed silica (CABOSIL TS-610) was slurried 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) to give a mixture. Using a spray dryer set at 160° C. and with an outlet temperature at 70° to 80° C., the mixture was introduced into an atomizing device of the spray dryer to produce droplets of the mixture, which were then contacted with a hot nitrogen gas stream to evaporate the liquid from the mixture to give a powder. The powder was separated from the gas mixture in a cyclone separator and the separated powder was discharged into a container as a fine powder. The resultant powder was slurried to give an activator formulation slurry form of a Catalyst System 4 ("AFS4") of 22 wt% solids in 10 wt% isoparaffin fluid and 68 wt% mineral oil.

[0084] 5. Preparation of Trim Catalyst Solution 1 ("TCS1").

[0085] 4.03 grams of solid powder Bis(2,4-di-*t*-butyl-6-isopropylamino phenoxy imine) zirconium dibenzyl (FI-A aka Formula I) were weighed into a first beaker. 568 grams of hexane were added to solid powder and mixed. The resulting solution was charged into a first cylinder. The first cylinder was transferred into a 106 liter (28 gallons) second cylinder. The second cylinder contained 572.03 grams of the mixture. 9.4 kg (20.8 pounds) of high purity isopentane was added to the 106 L cylinder to yield the Trim Catalyst Solution 1.

[0086] 6. Preparation of Trim Catalyst Solution 2 ("TCS2").

[0087] A solution of 0.04 wt % (methylcyclopentadienyl)(1,3-dimethyl-4,5,6,7-tetrahydroindenyl)zirconium dimethyl was prepared in isopentane (Formula IV).

[0088] 7. Preparation of Trim Catalyst Solution 3 ("TCS3"). (tetramethylcyclopentadienyl)(*n*-propylcyclopentadienyl)zirconium dimethyl.

[0089] 8. Preparation of Trim Catalyst Solution 4 ("TCS4") comprising a trim solution of cyclopentadienyl(1,5-dimethylindenyl) zirconium dimethyl (Formula V) was prepared in *n*-hexane and isopentane. (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V) and *n*-hexane were charged into a first cylinder. The resulting solution of (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V) solution in hexane from the first cylinder was charged into a 106 liter (28 gallons) second cylinder. The second cylinder contained 310 grams of 1.07 wt % (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V). 7.98 kg (17.6 pounds) of high purity isopentane was added to the 106 L cylinder to yield the Trim Catalyst Solution 4 of 0.04 wt % (cyclopentadienyl)(1,5-dimethylindenyl)zirconium dimethyl (Formula V) in *n*-hexane and isopentane.

[0090] 9. Polymerization Procedure

[0091] For Inventive Examples ("IE") 1-3 and Comparative Samples ("CS") CS1-3 described below, ethylene and 1-hexene were copolymerized using an Activator Formulation Slurry form of a Catalyst System and a controlled relative amount of a Trim Catalyst Solution in a fluidized bed-gas

phase polymerization (FB-GPP) reactor having a distribution grid to produce bimodal ethylene/hexene copolymer.

[0092] 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. Fluidized 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. 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. Feed streams of ethylene, nitrogen, and hydrogen were introduced 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 set the C_6/C_2 molar ratio and the H_2/C_2 molar ratio as specified.

[0093] Average copolymer residence time was from 1.9 to 4 hours. Concentrations of all gases 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 bimodal 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.

[0094] 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 was set to the feed of the Activator Formulation Slurry form of a Catalyst System to adjust the HLMI (I_{21}) of the produced bimodal 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 13 to about 20 kg/hour (about 28 to about 44 lbs/hr) of the bimodal ethylene/hexene copolymer.

[0095] Inventive Examples 1 to 3 (IE1, IE2, IE3): synthesized a bimodal ethylene/hexene copolymer using the Polymerization Procedure described above, wherein 1-alkene comonomer was 1-hexene, and Activator Formulation Slurry form of Catalyst System 1 (AFS1) and Trim Catalyst Solution 1 (TCS1).

[0096] Comparative Sample 1 (CS1): synthesized a bimodal ethylene/hexene copolymer using the Polymerization Procedure described above, wherein 1-alkene comonomer was 1-hexene, and Activator Formulation Slurry form of Catalyst System 2 (AFS2) and Trim Catalyst Solution 2 (TCS2).

[0097] Comparative Sample 2 (CS2): synthesized a bimodal ethylene/hexene copolymer using the Polymerization Procedure described above, wherein 1-alkene comonomer was 1-hexene, and Activator Formulation Slurry form of Catalyst System 3 (AFS3) and Trim Catalyst Solution 3 (TCS3).

[0098] Comparative Sample 3 (CS3): synthesized a bimodal ethylene/hexene copolymer using the Polymerization Procedure described above, wherein 1-alkene comonomer is 1-hexene, and Activator Formulation Slurry form of Catalyst System 4 (AFS4) and Trim Catalyst Solution 4 (TCS4).

Table 2 – Bimodal reactor conditions and bimodal polymer properties

	T (°C)	H2/C2 (mol ratio)	C6/C2 (mol ratio)	Iso- pentane %	Res time (hr)	Trim/Cat Ratio (lb/lb)	Density (g/cc)	I5	I21	Split (%HMW)	Mn	Mw	Mz	Mw/Mn	BBF	Vinyl	Olig, ppm
CS1 AFS2/TCS2	100	0.0023	0.0049	11.8	2.8	7.6	0.9495	0.21	6.4	39.6	20,666	309,822	1,983,288	14.99	1.18	Nm*	637
CS2 AFS3/TCS3	105	0.0020	0.0050	14.9	2.2	10.5	0.9483	0.17	5.7	49.6	17,322	349,270	2,218,986	20.16	1.30	Nm*	433
CS3 AFS4/TC4	95	0.0042	0.0071	11.1	4.1	3.5	0.9492	0.31	8.5	49.2	9,030	299,702	2,654,793	33.19	1.81	0.080	1185
IE1 AFS1/TCS1	100	0.0023	0.009	11.8	2.7	8.1	0.9491	0.26	6.8	53.7	19,773	307,753	2,909,311	15.56	1.35	0.669	8
IE2 AFS1/TCS1	100	0.0023	0.0085	11.8	1.9	7	0.9484	0.26	6.6	53.6	19,751	299,901	2,734,693	15.18	1.29	0.675	8
IE3 AFS1/TCS1	90	0.0040	0.0075	11.9	2.9	9.1	0.9485	0.41	8.1	56.5	20,278	259,378	2,354,495	12.79	1.29	0.625	15

[0099] Applicant discovered that a bimodal catalyst system of IE1, IE2, and IE3 with a phenoxy imine catalyst of Formula (I) or Formula (II) produces bimodal ethylene-based polymer, and bimodal ethylene/C₄-C₈ α -olefin copolymer in particular, with high HMW split (greater than 50% HMW, or from 51% to 75% HMW) and low oligomer content less than 300 ppm, or less than 100 ppm, or 1-50 ppm), at density greater than 0.940 g/cc, compared to CS1, CS2, and CS3.

[00100] 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) a first catalyst;
(B) a trim catalyst comprising a phenoxy imine catalyst selected from the 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
(C) at least one spray-dried methylaluminoxane activator.
2. The catalyst system of claim 1 wherein the first catalyst is selected from the group consisting of a non-metallocene catalyst and a metallocene catalyst.
3. The catalyst system of any of claims 1-2, wherein the first catalyst is spray-dried to a support.
4. The catalyst system of any of claims 1-3, wherein the first catalyst is spray-dried to a fused silica support.
5. The catalyst system of any of claims 1-4, wherein the trim catalyst is a solution of the phenoxy imine catalyst in an alkane hydrocarbon solvent.
6. The catalyst system of any of claims 1-5, wherein the phenoxy imine catalyst is unsupported.
7. A process comprising:
polymerizing ethylene with one or more olefins, under polymerization conditions, with a catalyst system comprising (A) a first catalyst, (B) 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 (C) at least one spray-dried methylaluminoxane activator; and
forming a bimodal ethylene/olefin terpolymer composition.

8. The process of claim 7, wherein the first catalyst is selected from the group consisting of a non-metallocene catalyst and a metallocene catalyst.
9. The process of any of claims 7-8, wherein the first catalyst is a non-metallocene catalyst.
10. The process of any of claims 7-9, wherein the olefin is selected from the group consisting of (i) 1-butene, (ii) 1-hexene (iii) 1-octene, and (iv) combinations thereof.
11. The process of any of claims 7-10, wherein the catalyst system comprises
 - (A) a non-metallocene catalyst spray-dried to a support,
 - (B) the 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,
 - (C) at least one spray-dried methylaluminoxane activator; and the process comprises forming a bimodal ethylene/olefin terpolymer composition.
12. The process of claim 11 wherein the polymerization conditions comprise a variable selected from the group consisting of
 - (i) a reaction temperature from 75°C to 105°C,
 - (ii) a molar ratio of the hydrogen gas to the ethylene from 0.0010 to 0.0070,
 - (iii) a molar ratio of the olefin to the ethylene from 0.0050 to 0.0300,
 - (iv) a reactor residence time from 1.0 hours to 4.5 hours, and
 - (v) combinations thereof.
13. The process of claim 12 comprising forming a bimodal ethylene/olefin terpolymer composition having (i) a HMW split greater than 50%.

14. The process of claim 13 comprising
forming a bimodal ethylene/olefin terpolymer composition having (ii) an oligomer
content less than 100 ppm.
15. The process of claim 14 comprising
forming a bimodal ethylene/olefin terpolymer composition having a property selected
from the group consisting of
- (iii) density from 0.935 g/cm³ to 0.950 g/cm³,
 - (iv) a molecular mass dispersity (M_w/M_n) from 12.5 to 16.0,
 - (v) a weight-average molecular weight (M_w) from 200,000 to 325,000,
 - (vi) a number-average molecular weight (M_n) from 15,000 to 25,000 g/mol,
 - (vii) a z-average molecular weight (M_z) from 2,000,000 to 3,000,000 g/mol,
 - (viii) a butyl branch frequency from 1.0 to 1.5 (1.29 to 1.35 butyl branches per 1000
carbon atom,
 - (ix) a vinyl content from 0.500 per 1000 carbon atom to 0.7 per 1000 carbon atom, and
 - (x) combinations thereof.