POLYOLEFIN COMPOSITIONS MADE WITH GERMANIUM BRIDGED GROUP IV METALLOCENES

Field of Disclosure

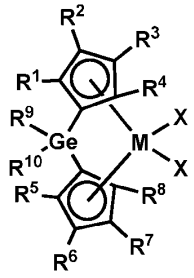
[0001] Embodiments of the present disclosure are directed towards polyolefin compositions made utilizing Ge bridged Group IV metallocenes, supported catalyst systems, and polyolefin compositions made utilizing supported catalyst systems, including spray-dried catalyst compositions of Ge bridged Group IV metallocenes.

Background

[0002] Polymers may be utilized for a number of products including films, fibers, pipes, nonwoven and/or woven fabrics, extruded articles, and/or molded articles, among others. Polymers can be formed by reacting one or more types of monomer in a polymerization reaction. There is continued focus in the industry on developing new and improved materials and/or processes that may be utilized to form polymers.

Summary

[0003] The present disclosure provides various embodiments, including the following. A polyolefin composition having from 50 to 99.9 wt % of units derived from ethylene based on a total weight of the polyolefin composition and from 1 to 50 wt% units derived from an α-olefin based on the total weight of the polyolefin composition, a weight average molecular weight from 30,000 to 400,000 g/mol, a melt temperature from 70 to 130 °C, a polydispersity index from 1.5 to 25.0, a melt index (I_2) from 0 to 1200 dg/min, a flow index (I_{21}) from 0.01 to 6000 dg/min, and from 0.0001 ppm to 10,000 ppm, based on the total weight of the polyolefin composition, of a deactivated Ge bridged Group IV metallocene represented by structure (I),



structure (I),

[0004] wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each

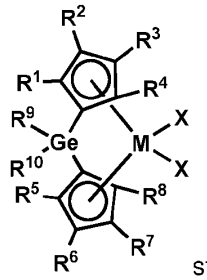
independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, M is a Group IV atom, and each X is independently a leaving group.

Detailed Description

[0005] Polyolefin compositions made utilizing supported Ge bridged Group IV metallocenes are discussed herein. Advantageously, these polyolefin compositions have a reverse comonomer distribution (defined when the MWCDI > 0) and one or more desirable properties, as compared to other compositions. For instance, the polyolefin compositions disclosed herein may surprisingly provide an improved, i.e. lesser, polydispersity index, an improved, i.e. greater, melt temperature, improved comonomer distribution (SCBD) or higher broad orthogonal comonomer distribution (BOCD), and/or an improved melt index, as compared to other supported catalyst compositions.

[0006] The polyolefin compositions disclosed herein can have from 50 to 99.9 wt % of units derived from ethylene based on a total weight of the polyolefin composition and from 0.1 to 50 wt% units derived from an α-olefin based on the total weight of the polyolefin composition, a weight average molecular weight from 30,000 to 400,000 g/mol, a melt temperature from 70 to 130 °C, a polydispersity index from 1.5 to 25.0, a melt index (I_2) from 0 to 1200 dg/min, a flow index (I_{21}) from 0.01 to 6000 dg/min, and from 0.0001 ppm to 10,000 ppm, based on the total weight of the polyolefin composition, of a deactivated Ge bridged Group IV metallocene.

[0007] One or more embodiments provide that the deactivated Ge bridged Group IV metallocene can be represented by structure (I)

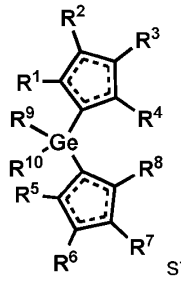


structure (I)

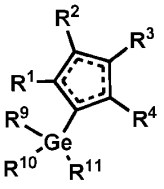
[0008] wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, M is a Group IV atom, and each X is independently a leaving group. The deactivated Ge bridged Group IV metallocene, as discussed herein, includes isomers thereof.

[0009] As used herein, “deactivated” refers to an inactive catalyst, e.g., catalytically inactive in polymerization. As used herein, “inactive” refers to an inability to polymerize ethylene as well as comonomer to produce subsequent ethylene and ethylene co-polymers. Activators, e.g., utilized for activation, are discussed further herein.

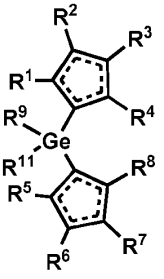
[0010] One or more embodiments provide that the deactivated Ge bridged Group IV metallocene can be non-ligated. The non-ligated deactivated Ge bridged Group IV metallocene can be neutralized and/or oxidized. As used herein, “neutralized” can refer to a protonated compound that is uncharged. As used herein, “oxidized” can refer to a reaction between the active catalyst and an oxidant, such as oxygen, an alcohol, an alkoxide or an inorganic salt of an alcohol, as well as a peroxide. The non-ligated deactivated Ge bridged Group IV metallocene can be represented by structure (II) and/or structure (III) and/or structure (IV), which each can also exist as multiple isomers;



structure (II),



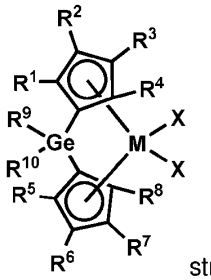
structure (III),



structure (IV),

[0011] wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen or a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, and R^{11} is a hydrogen, a peroxy (O-O), hydroxy, or a C1 to C10 alkoxy.

[0012] The polyolefin compositions disclosed herein can be made utilizing a Ge bridged Group IV metallocene represented by structure (I) that has been activated:



structure (I).

[0013] For structure (I), R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, M is a Group IV atom, and each X is independently a leaving group. Embodiments provide that the Ge bridged Group IV metallocene can be activated by utilizing an activator, as discussed further herein. Activators and activation are known.

[0014] For structure (I) M can be Ti. For structure (I) M can be selected from Zr and Hf. For structure (I) M can be Zr. For structure (I) M can be Hf.

[0015] For structure (I) X can be selected from alkyls and halogens. For structure (I) X can be Cl. For structure (I) X can be methyl.

[0016] As used herein, all reference to the Periodic Table of the Elements and groups thereof is to the NEW NOTATION published in HAWLEY'S CONDENSED CHEMICAL DICTIONARY, Thirteenth Edition, John Wiley & Sons, Inc., (1997) (reproduced there with permission from IUPAC), unless reference is made to the Previous IUPAC form noted with Roman numerals (also appearing in the same), or unless otherwise noted.

[0017] As used herein, an "alkyl" includes linear, branched and cyclic paraffin radicals that are deficient by one hydrogen. Thus, for example, CH_3 ("methyl") and CH_2CH_3 ("ethyl") are examples of alkyls.

[0018] As used herein, an "alkenyl" includes linear, branched and cyclic olefin radicals that are deficient by one hydrogen; alkynyl radicals include linear, branched and cyclic acetylene radicals deficient by one hydrogen radical.

[0019] As used herein, "aryl" groups include phenyl, naphthyl, pyridyl and other radicals whose molecules have the ring structure characteristic of benzene, naphthylene, phenanthrene, anthracene, etc. It is understood that an "aryl' group can be a C_6 to C_{20} aryl group. For example, a C_6H_5 aromatic structure is an "phenyl", a C_6H_4 2 aromatic structure is an "phenylene". An "arylalkyl" group is an alkyl group having an aryl group pendant therefrom. It is understood that an "aralkyl" group can be a C_7 to C_{20} aralkyl group. An "alkylaryl" is an aryl group having one or more alkyl groups pendant therefrom.

[0020] As used herein, "heteroaryl" groups include thiophene, furan, pyrrole, pyrazole, indole, imidazole, pyridine and other radicals whose molecules have the ring structure characteristic of these C3 to C30 heteroaryl motifs.

[0021] As used herein, an "alkylene" includes linear, branched and cyclic hydrocarbon radicals deficient by two hydrogens. Thus, CH_2 ("methylene") and CH_2CH_2 ("ethylene") are examples of alkylene groups. Other groups deficient by two hydrogen radicals include "arylene" and "alkenylene".

[0022] The Ge bridged Group IV metallocenes discussed herein can be made by processes, i.e. with conventional solvents, reaction conditions, reaction times, and isolation procedures, utilized for making known metallocenes.

[0023] As mentioned, the Ge bridged Group IV metallocenes can be utilized to make supported catalyst systems or compositions. In some embodiments the Ge bridged Group IV metallocene and support material are contacted together in an inert hydrocarbon liquid to give a suspension in the inert hydrocarbon liquid, then the suspension is contacted with the activator to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0024] In other embodiments the Ge bridged Group IV metallocene and activator are contacted together in an inert hydrocarbon liquid to give a solution of a catalyst in the

inert hydrocarbon liquid, then the solution is contacted with the support material to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0025] In other embodiments the activator and the support material are contacted together in an inert hydrocarbon liquid to give a suspension of a supported activator in the inert hydrocarbon liquid, then the suspension is contacted with the Ge bridged Group IV metallocene to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0026] In other embodiments the Ge bridged Group IV metallocene, activator, and support material are contacted together simultaneously in an inert hydrocarbon liquid to give a suspension of the supported catalyst, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[0027] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may include a step of decanting some of the inert hydrocarbon liquid from the suspension. In some embodiments the decanting method comprises pouring off excess inert hydrocarbon liquid from the suspension to give a concentrated suspension of the supported catalyst system.

[0028] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may comprise a step of drying the supported catalyst system. The drying step may comprise a conventional drying method or a spray-drying method.

[0029] A conventional drying method comprises a method of slowly increasing the mass or molar amount of less volatile chemical constituent(s) per unit volume of a continuous mixture comprising more volatile and less volatile chemical constituent(s) by gradually removing the more volatile chemical constituent(s) from the less volatile constituent(s) of the continuous mixture to give a concentrate having a higher mass or molar amount of the less volatile chemical constituent(s) per unit volume than did the continuous mixture, wherein the rate of gradual removing is limited by a relatively small evaporative surface area to mass ratio (compared to spray-drying). The concentrate may be a precipitated solid.

[0030] As mentioned, the Ge bridged Group IV metallocenes can be utilized to make spray-dried compositions, i.e., spray-dried Ge bridged Group IV metallocene compositions. As used herein, “spray-dried composition” refers to a composition that includes a number of components that have undergone a spray-drying process. Various

spray-drying process are known in the art and are suitable for forming the spray-dried compositions disclosed herein. One or more embodiments provide that the spray-dried composition comprises a trim composition.

[0031] In one or more embodiments, the spray-drying process may comprise atomizing a composition including the Ge bridged Group IV metallocene. A number of other known components may be utilized in the spray-drying process. An atomizer, such as an atomizing nozzle or a centrifugal high speed disc, for example, may be used to create a spray or dispersion of droplets of the composition. The droplets of the composition may then be rapidly dried by contact with an inert drying gas. The inert drying gas may be any gas that is non-reactive under the conditions employed during atomization, such as nitrogen, for example. The inert drying gas may meet the composition at the atomizer, which produces a droplet stream on a continuous basis. Dried particles of the composition may be trapped out of the process in a separator, such as a cyclone, for example, which can separate solids formed from a gaseous mixture of the drying gas, solvent, and other volatile components.

[0032] A spray-dried composition may have the form of a free-flowing powder, for instance. After the spray-drying process, the spray-dried composition and a number of known components may be utilized to form a slurry. The spray-dried composition may be utilized with a diluent to form a slurry suitable for use in olefin polymerization, for example. In one or more embodiments, the slurry may be combined with one or more additional catalysts or other known components prior to delivery into a polymerization reactor.

[0033] In one or more embodiments, the spray-dried composition may be formed by contacting a spray dried activator particle, such as spray dried fumed silica (*e.g.* Cabosil) and methylaluminoxane (MAO), with a solution of the Ge bridged Group IV metallocene. Such a solution of the Ge bridged Group IV metallocenes typically may be made in an inert hydrocarbon solvent, for instance, and is sometimes called a trim solution. Such a spray-dried composition comprised of contacting a trim solution of the Ge bridged Group IV metallocene with a spray dried activator particle, such as spray-dried MAO, may be made *in situ* in a feed line heading into a slurry or gas phase polymerization reactor by contacting the trim solution with a slurry, typically in mineral oil, of the spray-dried activator particle.

[0034] As an example, various spray-drying conditions may be utilized for different applications. For instance, the spray-drying process may utilize a drying

temperature from 115 to 185 °C. Various sizes of orifices of the atomizing nozzle employed during the spray-drying process may be utilized to obtain different particle sizes. Alternatively, for other types of atomizers such as discs, rotational speed, disc size, and number/size of holes may be adjusted to obtain different particle sizes. One or more embodiments provide that a filler may be utilized in the spray-drying process. Different fillers and amounts thereof may be utilized for various applications.

[0035] The spray-dried Ge bridged Group IV metallocene compositions may be utilized to make the polyolefin compositions disclosed herein. For instance, the Ge bridged Group IV metallocene may be activated, i.e. with an activator, to make a Ge bridged Group IV metallocene catalyst. One or more embodiments provide that the spray-dried compositions include 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, e.g., to provide the catalyst. The activator may also be referred to as a "co-catalyst". 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. Activators include methylaluminoxane (MAO) and modified methylaluminoxane (MMAO), among others. One or more embodiments provide that the activator is methylaluminoxane. Activating conditions are well known in the art. Known activating conditions may be utilized.

[0036] The activator used in the heterogenization method may be any compound capable of reacting with the precatalyst of formula (I) to yield an active olefin polymerization catalyst. The activator may be a Lewis acid, a non-coordinating ionic activator, or an ionizing activator, or a Lewis base.

[0037] A molar ratio of metal, e.g., aluminum, in the activator to Group IV metal in the Ge bridged Group IV metallocene may be 10000 : 1 to 0.5 : 1, 7000 : 1 to 0.5 : 1, 3500: 1 to 0.5: 1, 1500 : 1 to 0.5: 1, 750 : 1 to 0.5 : 1, 300 : 1 to 0.5 : 1, or 150: 1 to 1 : 1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 75:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 100:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 150:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV

metallocene is at least 300:1. One or more embodiments provide that the molar ratio of metal in the activator to Group IV metal in the Ge bridged Group IV metallocene is at least 750:1. Suitable activators are commercially available. In some embodiments the aluminum based activator is an alkylaluminum or an alkylaluminoxane (alkylalumoxane). Any alkyl group may be utilized. In some embodiments, each alkyl of the alkylaluminum or alkylaluminoxane independently may be a (C_1-C_8)alkyl, alternatively a (C_1-C_7)alkyl, alternatively a (C_1-C_6)alkyl, alternatively a (C_1-C_4)alkyl.

[0038] The alkylaluminum may be a trialkylaluminum, alkylaluminum halide, or alkylaluminum alkoxide (diethylaluminum ethoxide). The trialkylaluminum may be trimethylaluminum, triethylaluminum ("TEAl"), tripropylaluminum, or tris(2-methylpropyl)aluminum. The alkylaluminum halide may be diethylaluminum chloride. The alkylaluminum alkoxide may be diethylaluminum ethoxide.

[0039] The Ge bridged Group IV metallocenes, as well as a number of other components discussed herein, can be supported on the same or on separate supports, or one or more of the components may be used in an unsupported form. Utilizing the support may be accomplished by any technique used in the art. The support may be functionalized. The spray-dried compositions can include a support.

[0040] A "support", which may also be referred to as a "carrier", refers to any support material, including a porous support material, such as talc, inorganic oxides, and inorganic chlorides. 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.

[0041] Support materials include inorganic oxides that include Group 2, 3, 4, 5, 13 or 14 metal oxides. The terms "support", "solid support", "support material", and "solid support material" may be used interchangeably, and herein refer to a porous inorganic substance or organic substance. 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. An example of a support is fumed silica available under the trade name CABOSIL 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.

[0042] Embodiments provide that the inorganic oxide support material is porous and has variable surface area, pore volume, and average particle size. In some embodiments, the surface area is from 50 to 1000 square meter per gram (m^2/g) and the average particle size is from 1 to 300 micrometers (μm), alternatively 20 to 300 μm. Alternatively, the pore volume is from 0.5 to 6.0 cubic centimeters per gram (cm^3/g) and the surface area is from 200 to 600 m^2/g. Alternatively, the pore volume is from 1.1 to 1.8 cm^3/g and the surface area is from 245 to 375 m^2/g. Alternatively, the pore volume is from 2.4 to 3.7 cm^3/g and the surface area is from 410 to 620 m^2/g. Alternatively, the pore volume is from 0.9 to 1.4 cm^3/g and the surface area is from 390 to 590 m^2/g. Each of the above properties are measured using conventional techniques known in the art.

[0043] The support material may comprise silica, alternatively amorphous silica (not quartz), alternatively a high surface area amorphous silica, e.g., from 500 to 1000 m^2/g. Such silicas are commercially available from several sources including the Davison Chemical Division of W.R. Grace and Company, e.g., Davison 952 and Davison 955 products, and PQ Corporation, e.g., ES70 product. The silica may be in the form of spherical particles, which may be obtained by a spray-drying process. Alternatively, MS3050 product is a silica from PQ Corporation that is not spray-dried. As procured, these silicas are not calcined (i.e., not dehydrated). Silica that is calcined prior to purchase may also be used as the support material.

[0044] In some embodiments the solid support is a hydrophobic fumed silica. The hydrophobic fumed silica is made by contacting an untreated fumed silica, having surfaces containing silicon-bonded hydroxyl groups (Si-OH groups), with a hydrophobing agent, described later. In some embodiments the hydrophobing agent is a silicon-based hydrophobing agent, containing on average per molecule one or more functional groups reactive with a Si-OH group, to give the hydrophobic fumed silica. The silicon-based hydrophobing agent may be selected from $(CH_3)_2SiCl_2$, a polydimethylsiloxane, hexamethyldisilazane (HMDZ), and a $(C_1\text{-}C_{10})$alkylSi$((C_1\text{-}C_{10})$alkoxy$)_3$ (e.g., an octyltrialkoxysilane such as octyltriethoxysilane, i.e., $CH_3(CH_2)_7Si(OCH_2CH_3)_3$). In some embodiments the silicon-based hydrophobing agent is dimethyldichlorosilane, i.e.,

$(CH_3)_2SiCl_2$. In some embodiments the support material is a dimethyldichlorosilane-treated fumed silica, such as that sold as product TS-610 from Cabot Corporation.

[0045] The support material may be uncalcined or calcined. The calcined support material is made prior to being contacted with a precatalyst, activator, and/or hydrophobing agent, by heating the support material in air to give a calcined support material. The calcining comprises heating the support material at a peak temperature from 350 °C to 850 °C, alternatively from 400 °C to 800 °C, alternatively from 400 °C to 700 °C, alternatively from 500° to 650° C and for a time period from 2 to 24 hours, alternatively from 4 to 16 hours, alternatively from 8 to 12 hours, alternatively from 1 to 4 hours, thereby making the calcined support material. If the support material has not been heated in this way it is an uncalcined support material.

[0046] The Ge bridged Group IV metallocenes, e.g., the spray-dried Ge bridged Group IV metallocene compositions, and an olefin can be contacted under polymerization conditions to make the polyolefin compositions disclosed herein. The polymerization process may be a suspension polymerization process, a slurry polymerization process, and/or a gas phase polymerization process. The polymerization process may utilize using known equipment and reaction conditions, e.g., known polymerization conditions. The polymerization process is not limited to any specific type of polymerization system. The polyolefin compositions can be utilized for a number of articles such as films, fibers, pipes, nonwoven and/or woven fabrics, extruded articles, and/or molded articles.

[0047] One or more embodiments provide that the polyolefin compositions are made utilizing a gas-phase reactor system. One or more embodiments provide that a single gas-phase reactor, e.g., in contrast to a series of reactors, is utilized. In other words, polymerization reaction occurs in only one reactor. For instance, the polyolefin compositions can be made utilizing a fluidized bed reactor. Gas-phase reactors are known and known components may be utilized for the fluidized bed reactor.

[0048] As used herein an “olefin,” which may be referred to as an “alkene,” refers to a linear, branched, or cyclic compound including carbon and hydrogen and having at least one double bond. As used herein, when a polyolefin composition, polymer, and/or copolymer is referred to as comprising, e.g., being made from, an olefin, the olefin present is the polymerized form of the olefin. For example, when a polyolefin composition is said to have an ethylene content of 75 wt% to 95 wt%, it is understood that the polymer unit in the polyolefin composition is derived from ethylene in the

polymerization reaction(s) and the derived units are present at 75 wt% to 95 wt%, based upon the total weight of the polyolefin composition. A higher α-olefin refers to an α-olefin having 3 or more carbon atoms.

[0049] Polyolefin compositions made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can be made from olefin monomers such as ethylene, i.e., polyethylene, and linear or branched higher alpha-olefin monomers containing 3 to 20 carbon atoms. Examples of higher alpha-olefin monomers include, but are not limited to, propylene, butene, pentene, 1-hexene (which can be referred to more simply as hexene), and 1-octene. Examples of polyolefins include ethylene-based polyolefin compositions, having at least 50 wt % ethylene, including ethylene-1-butene, ethylene-1-hexene, and ethylene-1-octene copolymers, among others. One or more embodiments provide that the polyolefin composition can include from 50 to 99.9 wt % of units derived from ethylene based on a total weight of the polymer. All individual values and subranges from 50 to 99.9 wt % are included; for example, the polyolefin composition can include from a lower limit of 50, 60, 70, 80, or 90 wt % of units derived from ethylene to an upper limit of 99.9, 99.7, 99.4, 99, 96, 93, 90, or 85 wt % of units derived from ethylene based on the total weight of the polyolefin composition. The polyolefin composition can include from 0.1 to 50 wt % of units derived from comonomer, e.g., 1-hexene, based on the total weight of the polyolefin composition. One or more embodiments provide that 50 to 99 wt % of units are derived from ethylene based on a total weight of the polyolefin composition and from 1 to 50 wt% units are derived from 1-hexene based on the total weight of the polyolefin composition. One or more embodiments provide that ethylene is utilized as a monomer and 1-hexene is utilized as a comonomer. One or more embodiments provide that 70 to 95 wt % of units are derived from ethylene based on a total weight of the polyolefin composition and from 5 to 30 wt% units are derived from 1-hexene based on the total weight of the polyolefin composition.

[0050] The polyolefin compositions made with the spray-dried Ge bridged Group IV metallocene disclosed herein can be made in a fluidized bed reactor. The fluidized bed reactor can have a reaction temperature from 10 to 130 °C. All individual values and subranges from 10 to 130 °C are included; for example, the fluidized bed reactor can have a reaction temperature from a lower limit of 10, 20, 30, 40, 50, or 55 °C to an upper limit of 130, 120, 110, 100, 90, 80, 70, or 60 °C.

[0051] The fluidized bed reactor can have an ethylene partial pressure from 30 to 350 pounds per square inch (psi). All individual values and subranges from 30 to 350

are included; for example, the fluidized bed reactor can have an ethylene partial pressure from a lower limit of 30, 45, 60, 75, 85, 90, or 95 psi to an upper limit of 350, 300, 250, 240, 220, 200, 150, or 125 psi.

[0052] One or more embodiments provide that ethylene is utilized as a monomer and hexene is utilized as a comonomer. The fluidized bed reactor can have a comonomer to ethylene mole ratio, e.g., C_6/C_2, from 0.0001 to 0.100. All individual values and subranges from 0.0001 to 0.100 are included; for example, the fluidized bed reactor can have a comonomer to ethylene mole ratio from a lower limit of 0.0001, 0.0005, 0.0007, 0.001, 0.0015, 0.002, 0.007, or 0.010 to an upper limit of 0.100, 0.080, or 0.050.

[0053] When hydrogen is utilized for a polymerization process, the fluidized bed reactor can have a hydrogen to ethylene mole ratio (H_2/C_2) from 0.00001 to 1.80000, for instance. All individual values and subranges from 0.00001 to 1.80000 are included; for example, the fluidized bed reactor can have a H_2/C_2 from a lower limit of 0.00001, 0.00005, or 0.00008 to an upper limit of 1.80000, 1.20000, 0.90000, 0.500000, 0.10000, 0.01500, 0.00700, or 0.00500. One or more embodiments provide that hydrogen is not utilized.

[0054] The polyolefin compositions disclosed herein, e.g., made with the spray-dried Ge bridged Group IV metallocene compositions discussed herein, can have a reverse comonomer distribution. A reverse comonomer distribution is defined when the molecular weight comonomer distribution index is greater than 0, (MWCDI > 0), and a normal comonomer distribution is defined when the MWCDI < 0. When the MWCDI = 0 the comonomer distribution is said to be flat. Additionally, the MWCDI quantifies the magnitude of the comonomer distribution. Comparing two polymers that have MWCDI > 0, the polymer with the greater MWCDI value is defined to have a greater, i.e., increased, reverse comonomer distribution or increased broad orthogonal comonomer distribution (BOCD); in other words, the polymer with the greater MWCDI value has a greater reverse comonomer distribution. Polymers with a relatively greater MWCDI, i.e., BOCD, can provide one or more improved physical properties, as compared to polymers having a relatively lesser MWCDI. Surprisingly, the polyolefin composition provides an improved, i.e. greater, MWCDI, as compared to other compositions made with a Si bridged Group IV metallocene at the same polymerization conditions. MWCDI can be determined as discussed further herein.

[0055] The polyolefin compositions disclosed herein, e.g., made with the spray-dried Ge bridged Group IV metallocene compositions discussed herein, can have a weight average molecular weight (Mw) from 30,000 to 400,000 g/mol. All individual values and subranges from 30,000 to 400,000 g/mol, are included; for example, the polyolefin composition can have an Mw from a lower limit of 30,000, 45,000, or 50,000 g/mol to an upper limit of 400,000, 350,000, 300,000, 250,000, or 190,000 g/mol. Mw can be determined by gel permeation chromatography (GPC), as is known in the art. GPC is discussed herein.

[0056] The polyolefin compositions disclosed herein, e.g., made with the spray-dried Ge bridged Group IV metallocene compositions discussed herein, can have a density from 0.8700 to 0.9700 g/cm^3. All individual values and subranges from 0.8700 to 0.9700 g/cm^3 are included; for example, the polyolefin composition can have a density from a lower limit of 0.8700, 0.9000, 0.9100, 0.9150, 0.9200, or 0.9250 g/cm^3 to an upper limit of 0.9700, 0.9600, 0.9500, 0.9450, 0.9350, or 0.9300 g/cm^3. Density can be determined by according to ASTM D792.

[0057] The polyolefin compositions disclosed herein, e.g., made with the spray-dried Ge bridged Group IV metallocene compositions discussed herein, can have a melt index (I_2) from 0 to 1200 dg/min. I_2 can be determined according to ASTM-1238, Condition B (190 °C, 2.16 kg). All individual values and subranges from 0 to 1200 dg/min are included; for example, the polymer can have an I_2 from a lower limit of 0, 0.05, 0.07, 0.10, 0.20, or 0.30 dg/min to an upper limit of 1200, 600, 400, 375, or 350 dg/min.

[0058] The polymers made with the spray-dried Ge bridged Group IV metallocene compositions disclosed herein can have a flow index (I_{21}) from 0.01 to 6000 dg/min. I_{21} can be determined according to ASTM-1238, Condition B (190 °C, 21.6 kg). All individual values and subranges from 0.01 to 6000 dg/min are included; for example, the polymer can have an I_{21} from a lower limit of 0.01, 0.05, 0.10 or 0.50 dg/min to an upper limit of 6000, 1200, 400, 375, or 350 dg/min. Providing a broad range for melt index (I_2) and flow index (I_{21}) is advantageous for a number of applications.

[0059] One or more embodiments provide that the polyolefin composition has a melt index (I_2) from 5 to 120 dg/min when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 100 °C and utilizing an H2/C2 ratio of 0.002.

[0060] One or more embodiments provide that the polyolefin composition has a melt index (I_2) from 0 to 5.0 dg/min when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 100 °C and utilizing a H2/C2 ratio of 0.0005.

[0061] The polyolefin compositions disclosed herein, e.g., made with the spray-dried Ge bridged Group IV metallocene compositions discussed herein, can have a polydispersity index (Mw/Mn) from 1.5 to 25.0. Polydispersity index can be determined according to GPC, as discussed herein. All individual values and subranges from 1.5 to 25.0 are included; for example, the polyolefin compositions can have a polydispersity index from a lower limit of 1.5, 2.0 or 3.0 to an upper limit of 25.0, 23.0, or 22.0. Surprisingly, the polyolefin composition provides a decreased or narrowed, polydispersity index, as compared to other compositions made with a Si bridged Group IV metallocene at the same polymerization conditions, which can provide more catalyst and/or polyethylene resin design degrees of freedom along with enhanced polyethylene product performance.

[0062] One or more embodiments provide that the polyolefin composition has a polydispersity index from 2 to 6 when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 110 °C and utilizing a H_2/C_2 ratio of 0 to 0.002, a C_6/C_2 ratio of 0 to 0.02, and an ethylene partial pressure up to 350 psi.

[0063] One or more embodiments provide that the polyolefin composition has a polydispersity index from 3.0 to 6.0 when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 100 °C and utilizing a H2/C2 ratio of 0.002.

[0064] The polyolefin compositions disclosed herein, e.g., made with the spray-dried Ge bridged Group IV metallocene compositions discussed herein, can have a melt temperature from 70 to 140 °C. Melt temperature can be determined via Differential Scanning Calorimetry according to ASTM D 3418-08. In general, a scan rate of 10° C/min on a sample (10 mg) can be used, and the second heating cycle can be used to determine Tm. All individual values and subranges from 70 to 140 °C are included; for example, the polyolefin compositions can have a melt temperature from a lower limit of 70, 71, or 72 °C to an upper limit of 140, 135, or 130 °C.

[0065] One or more embodiments provide that the polyolefin composition has a melt temperature from 120 to 130 °C when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 100 °C and utilizing a H2/C2 ratio of 0.002.

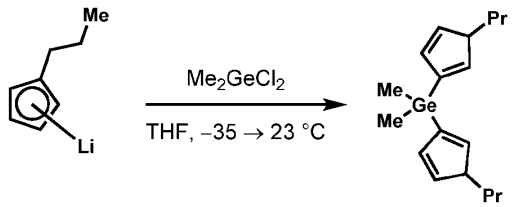
[0066] One or more embodiments provide that the polyolefin composition has a melt temperature from 115 to 125 °C when made in a gas phase polymerization reactor having a reaction temperature of 80 °C and utilizing a H2/C2 ratio of 0.0005 and a C6/C2 ratio of 0.01.

[0067] When the polyolefin compositions made are with the activated spray-dried Ge bridged Group IV metallocene discussed herein, the polyolefin composition can include from 0.0001 ppm to 10,000 ppm of a deactivated Ge bridged Group IV metallocene, e.g., represented by structure (I), (II), (III), and/or (IV). All individual values and subranges from 0.0001 ppm to 10,000 ppm are included; for example, the polyolefin compositions can include from a lower limit of 0.0001, 0.001, or 0.01 ppm to an upper limit of 10,000, 5,000, 1,000 or 500 ppm of deactivated Ge bridged Group IV metallocene, as discussed herein. The amount, e.g., ppm, of the deactivated Ge bridged Group IV metallocene can be determined by calculating the amount (mass) of polymer produced or calculated to be produced using ethylene and comonomer uptake, or consumption, divided by the amount (mass) of active Group IV catalyst used, and then multiplied by 1,000,000.

[0068] The deactivated Ge bridged Group IV metallocene, as discussed herein, is made from a polymerization process, as discussed herein, which utilizes the activated Ge bridged Group IV metallocene represented by structure (I). In other words, when making the polyolefin compositions disclosed herein, the activated Ge bridged Group IV metallocene can be subjected to polymerization conditions, including conditions during or after the polymerization process, to make the deactivated form of the Ge bridged Group IV metallocene from the activated Ge bridged Group IV metallocene.

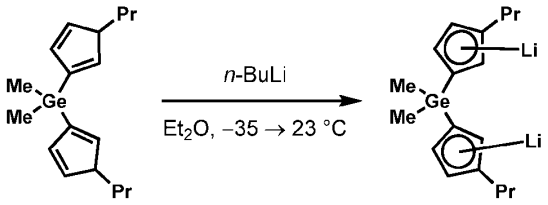
[0069] The polyolefin compositions disclosed herein are useful for a number of applications.

EXAMPLES

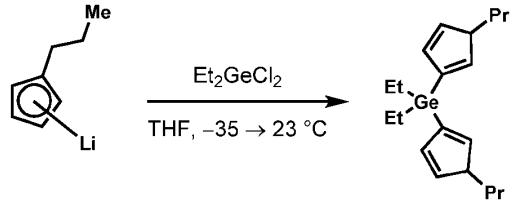


[0070] In a continuous purge nitrogen filled glovebox, a red-orange mixture of PrCpLi (0.250 g, 2.191 mmol, 2.25 eq) in anhydrous deoxygenated THF (15 mL) was

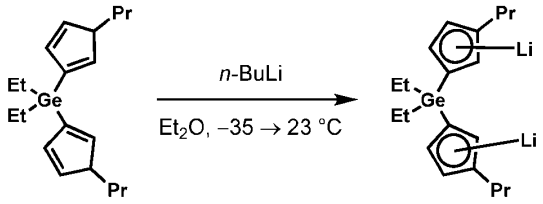
placed in a freezer (-35 °C) for 12 hrs, and then neat Me2GeCl2 (0.11 mL, 0.9738 mmol, 1.00 eq) was added. The red-orange mixture was allowed to sit in the freezer for 30 mins, removed, and the red-orange solution was stirred (500 rpm) at 23 °C for 4 hrs. The solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 3 mL), and concentrated to provide the bridged bis-cyclopentadiene, which was observed to be a clear golden yellow oil (0.303 g, 0.9524 mmol, 98%). NMR indicated product exists as a mixture of isomers. ^{1}H NMR (400 MHz, C_6D_6) δ 6.82 – 5.91 (m, 6H), 4.31 – 2.83 (m, 2H), 2.39 (t, J = 7.6 Hz, 4H), 1.57 (h, J = 7.4 Hz, 4H), 0.92 (t, J = 7.4 Hz, 6H), -0.08 (s, 6H).



[0071] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.303 g, 0.9524 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 16 hrs, and then *n*-BuLi (0.86 mL, 2.143 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 30 mins, removed from the freezer, and stirred (500 rpm) at 23 °C for 2 hrs. The white mixture was suction filtered, the white solid was rinsed with Et_2O (4 x 10 mL), and dried *in vacuo* to provide the dilithio salt, which was observed to be a white solid (0.273 g, 0.8269 mmol, 87%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (400 MHz, C_6D_6 with THF) δ 6.05 – 6.02 (m, 2H), 5.94 (t, *J* = 2.1 Hz, 2H), 5.91 (t, *J* = 2.6 Hz, 2H), 2.69 – 2.60 (m, 4H), 1.75 – 1.66 (m, 4H), 1.05 – 0.99 (m, 6H), 0.63 (s, 6H).

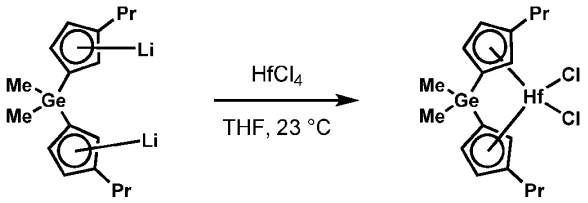


[0072] In a continuous purge nitrogen filled glovebox, a red-orange mixture of PrCpLi (0.250 g, 2.191 mmol, 2.25 eq) in anhydrous deoxygenated THF (20 mL) was placed in a freezer (-35 °C) for 12 hrs, and then neat Et_2GeCl_2 (0.14 mL, 0.9738 mmol, 1.00 eq) was added. The red-orange mixture was maintained in the freezer for 30 mins, removed, and the red-orange solution was stirred (500 rpm) at 23 °C for 4 hrs. The solution was concentrated, suspended in hexanes (5 mL), and concentrated. The mixture was suspended in hexanes (10 mL), stirred (500 rpm) for 2 mins, suction filtered through Celite, rinsed with hexanes (4 x 10 mL), concentrated, the filtrate was suspended in hexanes (10 mL), filtered through a double 0.45 µm PTFE filter, rinsed with hexanes (3 x 5 mL), and concentrated to provide the bridged bis-cyclopentadiene, which was observed to be a clear amber oil (0.318 g, 0.9186 mmol, 94%). NMR indicated product exists as a mixture of isomers. ^{1}H NMR (400 MHz, C_6D_6) δ 6.84 – 5.87 (m, 6H), 4.00 – 3.50 (br s, 2H), 2.50 – 2.36 (m, 4H), 1.59 (h, J = 7.4 Hz, 4H), 0.99 – 0.92 (m, 12H), 0.59 (q, J = 8.0 Hz, 4H).



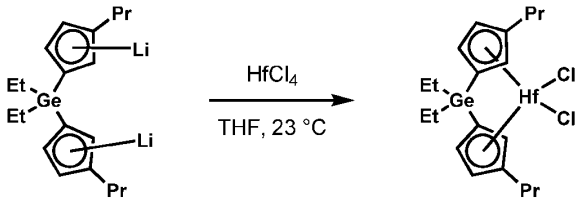
[0073] In a continuous purge nitrogen filled glovebox, a pale golden yellow solution of the starting bis-cyclopentadiene (0.318 g, 0.9186 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 2.5 hrs, and then *n*-BuLi (0.83 mL, 2.067 mmol, 2.25 eq, 2.5 M in hexanes) was added. The resultant white heterogeneous mixture was maintained in the freezer for 30 mins, removed from the freezer, and stirred (500 rpm) at 23 °C for 3 hrs. The white mixture was suction filtered, the white solid was rinsed with Et_2O (4 x 10 mL), and dried with vacuum to provide the dilithio salt as a white solid (0.280 g, 0.7817 mmol, 85%). NMR (in THF & C_6D_6) indicated product. ^{1}H NMR (400 MHz, C_6D_6) δ 6.15 (dd, J = 2.9, 2.1 Hz, 2H), 6.07 (t, J = 2.1 Hz, 2H), 6.05 – 6.01 (m, 2H), 2.77 – 2.66 (m, 4H), 1.83 – 1.69 (m, 4H), 1.44 – 1.36 (m, 6H), 1.28 – 1.19 (m, 6H), 1.06 (td, J = 7.2, 1.9 Hz, 4H).

[0074] Metallocene 1, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Hf, and each X is Cl, was made as follows.



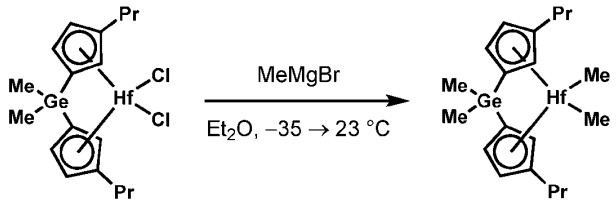
[0075] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $HfCl_4$ (92.8 mg, 0.2896 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.3040 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant pale-golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to afford the dichloride complex as a clear pale-yellow oil (95.4 mg, 0.1686 mmol, 58%). NMR indicated product exists as a mixture of *rac*- and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. ^{1}H NMR (500 MHz, C_6D_6) δ 6.59 – 6.56 (m, 2H), *6.53 – 6.49 (m, 2H), *5.57 (t, J = 2.7 Hz, 2H), 5.43 (t, J = 2.7 Hz, 2H), 5.25 (t, J = 2.4 Hz, 2H), *5.16 (t, J = 2.3 Hz, 2H), 2.88 – 2.70 (m, 4H), 1.61 – 1.47 (m, 4H), 0.87 (td, J = 7.4, 5.5 Hz, 6H), *0.33 (s, 3H), 0.29 (s, 6H), 0.26 (s, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ *140.01, 139.99, *125.30, 124.83, *111.29, 111.22, *110.74, 110.43, *107.83, 107.70, 32.25, *23.67, 23.62, 13.85, *13.83, *-6.18, -6.22, *-6.24.

[0076] Metallocene 2, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C2 alkyl, M is Hf, and each X is Cl, was made as follows.



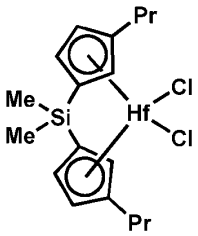
[0077] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $HfCl_4$ (85.2 mg, 0.2659 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (100.0 mg, 0.2792 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant golden yellow solution was stirred (500 rpm) for 18 hrs. The resultant pale-yellow solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden yellow amorphous foam was suspended in hexanes (10 mL), suction filtered through a fritted filter, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant pale-golden yellow oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant golden yellow oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered cold using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to afford the dichloride complex as a clear pale golden brown oil (0.156 g, 0.2633 mmol, 99%). NMR indicated product exists as a mixture of *rac*- and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. ^{1}H NMR (500 MHz, C_6D_6) δ 6.59 (dd, J = 2.8, 2.0 Hz, 2H), *6.53 (dd, J = 2.8, 2.1 Hz, 2H), *5.63 (t, J = 2.7 Hz, 2H), 5.49 (t, J = 2.7 Hz, 2H), 5.32 (t, J = 2.3 Hz, 2H), 5.24 (t, J = 2.4 Hz, 2H), 2.89 – 2.72 (m, 4H), 1.62 – 1.46 (m, 4H), 1.03 – 0.95 (m, 10H), 0.87 (td, J = 7.3, 5.4 Hz, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 140.02, *139.92, *125.51, 125.40, 112.05, *111.87, *111.57, 111.13, *106.88, 106.76, 32.28, *32.27, *23.68, 23.64, 13.89, *13.86, 8.25, *3.10, 3.05, *3.02.

[0078] Metallocene 3, a Ge bridged Group IV metallocene, corresponding to structure (1), where R^1, R^2, and R^4 are each H, R^3 is a C3 alkyl, R^5, R^6, and R^8 are each H, R^7 is a C3 alkyl, R^9 and R^{10} are each a C1 alkyl, M is Hf, and each X is Me, was made as follows.

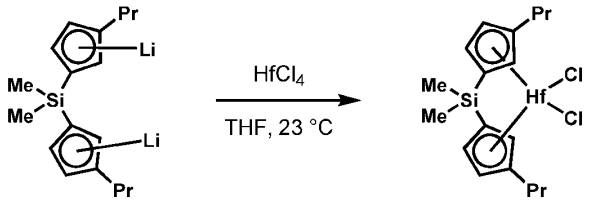


[0079] In a continuous purge nitrogen filled glovebox, a solution of the dichloride (90.2 mg, 0.1594 mmol, 1.00 eq) in anhydrous deoxygenated Et_2O (10 mL) was placed in a freezer (-35 °C) for 16 hrs, a solution of MeMgBr (0.13 mL, 0.3665 mmol, 2.30 eq, 3.0 M in Et_2O) was then added in a quick dropwise manner, the pale golden brown solution was removed from the freezer, stirred (500 rpm) at 23 °C for 8 hrs, and concentrated. Pentane (10 mL) was added, the mixture was stirred for 2 mins, filtered using a double 0.45 µm PTFE filter, rinsed with pentane (4 x 5 mL), and concentrated. The resultant pale yellow oil was diluted in pentane (5 mL), filtered using a double 0.45 µm PTFE filter, rinsed with pentane (4 x 5 mL), and concentrated to afford the dimethyl complex as a clear colorless oil (76.6 mg, 0.1456 mmol, 91%). NMR indicated product exists as a mixture of *rac*- and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. ^{1}H NMR (400 MHz, C_6D_6) δ 6.38 (dt, J = 6.5, 2.4 Hz, 2H), *5.41 (t, J = 2.7 Hz, 2H), 5.33 (t, J = 2.6 Hz, 2H), 5.21 (t, J = 2.3 Hz, 2H), *5.17 (t, J = 2.2 Hz, 2H), 2.68 – 2.50 (m, 4H), 1.62 (qd, J = 7.5, 1.3 Hz, 4H), 0.95 (td, J = 7.4, 2.9 Hz, 6H), *0.33 (s, 3H), 0.31 (s, 6H), *0.29 (s, 3H), *-0.24 (s, 3H), -0.32 (s, 6H), *-0.38 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 133.10, *132.97, *118.89, 118.67, 110.67, *110.64, *110.31, 110.04, *100.75, 100.69, 37.30, 32.07, *24.78, 24.75, 13.87, *13.86, *-5.88, -6.02, *-6.13.

[0080] Comparative Metallocene A may be represented by the following structure:



[0081] Comparative Metallocene A was made as follows.



[0082] In a continuous purge nitrogen filled glovebox, to a stirring (500 rpm) slurry of $HfCl_4$ (0.166 g, 0.5191 mmol, 1.00 eq) in anhydrous deoxygenated THF (10 mL) was added a solution of the dilithio salt (0.155 g, 0.5451 mmol, 1.05 eq) in THF (4 mL, rinse 3 x 2 mL). The resultant canary yellow solution was stirred (500 rpm) for 18 hrs. The resultant golden brown solution was concentrated, suspended in hexanes (10 mL), stirred (500 rpm) for 5 mins, suction filtered, rinsed with hexanes (4 x 10 mL), concentrated, the resultant golden brown amorphous foam was suspended in hexanes (10 mL), suction filtered, rinsed with hexanes (4 x 10 mL), and concentrated. The resultant golden brown amorphous oil was suspended in pentane (10 mL), placed in the freezer (-35 °C) for 4 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (3 x 5 mL), and concentrated. The resultant pale golden brown oil was suspended in pentane (10 mL), placed in the freezer for 18 hrs, filtered using a double 0.45 µm PTFE filter, rinsed with cold pentane (4 x 5 mL), and concentrated to afford the dichloride complex as a pale brown oil (0.157 g, 0.3019 mmol, 58%). NMR indicated product exists as a mixture of *rac*- and *meso* isomers. *Denotes chemical shifts of the *meso* isomer. ^{1}H NMR (400 MHz, C_6D_6) δ 6.57 (t, J = 2.4 Hz, 2H), *6.49 (t, J = 2.4 Hz, 2H), *5.56 (t, J = 2.8 Hz, 2H), 5.41 (t, J = 2.8 Hz, 2H), 5.23 (t, J = 2.3 Hz, 2H), *5.12 (t, J = 2.4 Hz, 2H), 2.86 – 2.65 (m, 4H), 1.61 – 1.44 (m, 4H), 0.86 (td, J = 7.3, 4.5 Hz, 6H), *0.22 (s, 3H), 0.19 (s, 6H), *0.16 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ *141.01, 140.67, *125.66, 125.46, *112.25, 112.03, 110.98, *110.96, *107.22, 107.10, *32.11, 32.07, *23.55, 23.50, 13.83, *13.81, *-5.86, -5.94, *-6.02.

[0083] Spray-dried Ge bridged Group IV metallocene composition 1 (SD Comp 1), was made as follows. In a nitrogen-purged glovebox, hydrophobic fumed silica (CAB-O-SIL TS-610; 1.815 grams) and toluene (37.5 grams) were added to a container and mixed, followed by addition of a 10 % solution (14.60 grams) by weight of methylaluminoxane (MAO) in toluene. Then the contents of the container were stirred for approximately 15 minutes. Then, Metallocene 1 (0.095 grams) was added to the container and the contents of the container were stirred for approximately 45 minutes. Then, the contents of the container were spray-dried utilizing a Buchi Mini Spray Drier B-

290 (140 °C set temperature; 75 °C outlet temperature; 150 rpm pump speed) to provide Spray-dried Ge bridged Group IV metallocene composition 1.

[0084] Spray-dried Ge bridged Group IV metallocene compositions 1, 2, 3 and 4 (SD Comp 1, 2, 3 and 4) and Comparative Spray-dried compositon A (SD Comp A) were made as Spray-dried Ge bridged Group IV metallocene composition 1 with changes shown in Table 1.

Table 1

Spray-dried composition	Metallocene	Fumed silica	10 % MAO solution	Toluene
Spray-dried Ge bridged Group IV metallocene composition 1	Metallocene 1 0.095 g	1.815 g	14.60 g	37.5 g
Spray-dried Ge bridged Group IV metallocene composition 2	Metallocene 2 0.071 g	1.295 g	10.40 g	37.5 g
Spray-dried Ge bridged Group IV metallocene composition 3	Metallocene 1 0.018 g	0.583 g	4.60 g	37.5 g
Spray-dried Ge bridged Group IV metallocene composition 4	Metallocene 3 0.045 g	1.570 g	12.35 g	75 g
Comparative Spray-dried compostion A	Comparative Metallocene A 0.064 g	1.340 g	10.70 g	37.5 g

[0085] Polyolefin compositions were made respectively utilizing Spray-dried Ge bridged Group IV metallocene compositions 1-2 and Comparative Spray-dried compostion B as follows. For respective polymerizations, a lab-scale gas phase polymerization reactor (2-liter, stainless steel autoclave equipped with a variable speed mechanical agitator) was charged with dried NaCl (200 g) and heated to 100 °C under a stream of nitrogen for one hour. Then the reactor was purged with nitrogen, silica

supported methylaluminoxane was added as a scavenger to the reactor, the reactor temperature was adjusted to approximately a desired temperature, and the contents of the reactor were stirred (350 rpm). The reactor was preloaded with hydrogen, ethylene, and 1-hexene to a desired pressure, hydrogen / ethylene molar ratio (H_2/C_2), and 1-hexene / ethylene molar ratio (C_6/C_2). Upon reaching steady state, catalyst was charged into the reactor (at a temperature indicated below) to start polymerization. The reactor temperature was maintained at a desired temperature for the 60-minute polymerization, where the H_2/C_2 ratio, C_6/C_2 ratio and ethylene partial pressure (C2PP) were maintained constant. At the end of the 60-minute polymerization, the reactor was cooled down, vented and opened. The resulting mixture was washed with water and methanol, and dried. Polymerization conditions and a number of properties are reported in the following Tables.

Table 2

Polyolefin composition	Spray-dried composition	Reactor Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Deactivated metallocene (ppm)
Ex. 1	SD Comp. 1	80	0.01	0.0005	1.9	23.3	9,400	1,049,000	3.0
Ex. 2	SD Comp. 3	80	0.01	0.0005	3.0	17.0	5,900	1,101,800	2.9
Ex. 3	SD Comp. 4	80	0.01	0.0005	3.2	19.3	5,000	933,700	3.2
Comp. Ex. A	SD Comp. A	80	0.01	0.0005	5.3	4.4	2,600	291,000	10.0

Table 3

Polyolefin composition	Spray-dried composition	Reactor Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Deactivated metallocene (ppm)
Ex. 4	SD Comp 2	80	0.004	0.002	2.6	40.0	16,700	1,871,100	1.7
Comp. Ex. B	SD Comp A	80	0.004	0.002	5.0	41.7	7,100	795,500	3.7

Table 4

Polyolefin composition	Spray-dried composition	Reactor Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Deactivated metallocene (ppm)
Ex. 5	SD Comp 1	80	0.02	0.0005	1.9	40.9	17,000	1,907,000	1.7
Comp. Ex. C	SD Comp A	80	0.02	0.0005	5.1	20.8	2,200	246,500	11.8

Table 5

Polyolefin composition	Spray-dried composition	Reactor Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Deactivated metallocene (ppm)
Ex. 6	SD Comp	90	0.02	0.0005	2.2	43.8	16,900	1,896,400	1.7

	1								
Ex. 7	SD Comp 2	90	0.02	0.0005	2.3	31.1	29,900	3,350,900	1.0
Comp. Ex. D	SD Comp A	90	0.02	0.0005	5.0	14.9	1,700	190,500	15.3

Table 6

Polyolefin composition	Spray-dried composition	Reactor Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Deactivated metallocene (ppm)
Ex. 8	SD Comp 2	100	0.004	0.002	2.2	19.8	22,700	2,543,400	1.3
Ex. 9	SD Comp. 3	100	0.004	0.002	3.2	16.8	23,400	4,369,700	0.7
Ex. 10	SD Comp. 4	100	0.004	0.002	2.8	49.5	19,900	3,716,200	0.8
Comp. Ex. E	SD Comp A	100	0.004	0.002	3.0	49.2	15,300	1,714,300	1.7

Table 7

Polyolefin composition	Spray-dried composition	Reactor Temp (°C)	C_6/C_2	H_2/C_2	Charge (mg)	Yield (g)	Productivity	Efficiency	Deactivated metallocene (ppm)
Ex. 11	SD Comp 1	80	0.016	0.0005	2.5	40.8	25,100	2,812,300	1.1
Ex. 12	SD Comp. 2	80	0.016	0.0005	2.3	25.5	17,100	1,916,000	1.7
Ex. 13	SD Comp.	80	0.016	0.0005	3.3	27.7	6,900	1,288,500	2.6

	3								
Ex. 14	SD Comp 4	80	0.016	0.0005	2.8	17.8	13,300	2,483,700	1.2

Table 8

Properties corresponding to polyolefin compositions of Table 2								
Polyolefin composition	Mp (g /mol)	Mw (g /mol)	Poly dispersity index	C6 (wt %)	Tm (°C)	MWCDI	Melt Index (dg/min)	Deactivated metallocene (ppm)
Ex. 1	67,100	113,700	12.6	6.2	120	2.9	2.2	3.0
Ex. 2	72,400	238,600	6.5	6.6	120	2.4	No Flow	2.9
Ex. 3	86,800	242,700	5.3	7.0	118	2.2	No Flow	3.4
Comp. Ex. A	104,500	294,600	28.8	12.2	110	2.1	-	10.0

[0086] The data of Table 8 show that Examples 1, 2, and 3 had an improved, i.e. lesser, polydispersity index (PDI), as compared to Comparative Example A.

[0087] The data of Table 8 show that Examples 1, 2, and 3 had a greater melt temperature, as compared to Comparative Example A.

[0088] The data of Table 8 show that Examples 1, 2, and 3 had an improved, i.e. greater, MWCDI, as compared to Comparative Example A.

Table 9

Properties corresponding to polyolefin compositions of Table 3									
Polyolefin composition	M.I. (I2)	F.I. (I21)	Mp (g /mol)	Mw (g /mol)	PDI	C6 (wt %)	Tm (°C)	ΔH (J/g)	MWCDI
Ex. 4	107	766	30,100	51,900	4.1	3.3	126	152	0.6
Comp. Ex. A	25	285	35,500	75,900	10.4	3.2	125	143	0.4

[0089] The data of Table 9 show that Example 4 had an improved, i.e. lesser, polydispersity index, as compared to Comparative Example A.

[0090] The data of Table 9 show that Example 4 had a greater melt index, as compared to Comparative Example A.

[0091] The data of Table 9 show that Example 4 had an improved, i.e. greater, MWCDI, as compared to Comparative Example A.

Table 10

Properties corresponding to polyolefin compositions of Table 4									
Polyolefin composition	M.I. (I2)	F.I. (I21)	Mp (g /mol)	Mw (g /mol)	PDI	C6 (wt %)	Tm (°C)	ΔH (J/g)	MWCDI
Ex. 5	0.27	6.7	117,500	170,500	3.4	24.5	73	52	5.4
Comp. Ex. C	0.11	7.7	105,400	161,000	13.5	29.9	62	41	2.6

[0092] The data of Table 10 show that Example 5 had an improved, i.e. lesser, polydispersity index, as compared to Comparative Example C.

[0093] The data of Table 10 show that Example 5 had an improved, i.e. greater, melt temperature, as compared to Comparative Example C.

[0094] The data of Table 10 show that Example 5 had a greater melt index as compared to Comparative Example C.

[0095] The data of Table 10 show that Example 5 had an improved, i.e. greater, MWCDI, as compared to Comparative Example C.

Table 11

Properties corresponding to polyolefin compositions of Table 5									
Polyolefin composition	M.I. (I2)	F.I. (I21)	Mp (g /mol)	Mw (g /mol)	PDI	C6 (wt %)	Tm (°C)	ΔH (J/g)	MWCDI
Ex. 6	0.37	7.3	113,500	182,500	21.1	19.6	-.	-	3.9
Ex. 7	0.74	13	108,400	168,600	4.0	18.6	86	69	4.3
Comp. Ex. D	No Flow	3.9	114,300	248,500	21.6	23.8	74	56	0.8

[0096] The data of Table 11 show that each of Example 6 and Example 7 had an improved, i.e. lesser, polydispersity index, as compared to Comparative Example D.

[0097] The data of Table 11 show that Example 7 had an improved, i.e. greater, melt temperature, as compared to Comparative Example D.

[0098] The data of Table 11 show that each of Example 6 and Example 7 had a greater melt index, as compared to Comparative Example D, which had no flow.

[0099] The data of Table 11 show that each of Example 6 and Example 7 had an improved, i.e. greater, MWCDI, as compared to Comparative Example D.

Table 12

Properties corresponding to polyolefin compositions of Table 6									
Polyolefin composition	M.I. (I2)	F.I. (I21)	Mp (g /mol)	Mw (g /mol)	PDI	C6 (wt %)	Tm (°C)	ΔH (J/g)	MWCDI
Ex. 8	20	281	40,000	70,100	3.7	2.9	124	154	0.7
Ex. 9	5.2	183	41,900	79,800	4.3	4.3	122	154	0.5
Ex. 10	12	295	40,600	97,600	5.2	3.9	123	151	0.4
Comp. Ex. E	11	163	47,600	99,000	13.3	3.6	123	127	0.4

[00100] The data of Table 12 show that Examples 8, 9, and 10 had an improved, i.e. lesser, polydispersity index, as compared to Comparative Example E.

[00101] The data of Table 12 show that Example 9 had a lower melt index, as compared to Comparative Example E.

[00102] The data of Table 12 show that Examples 8 and 10 had a greater melt index as compared to Comparative Example E.

[00103] The data of Table 12 show that Examples 8 and 10 had an improved, i.e. greater, MWCDI, as compared to Comparative Example E.

Table 13

Properties corresponding to polyolefin compositions of Table 7

Polyolefin composition	M.I. (I2)	F.I. (I21)	Mp (g /mol)	Mw (g /mol)	PDI	C6 (wt %)	Tm (°C)	ΔH (J/g)	MWCDI
Ex. 11	0.42	2.9	128,800	194,700	3.6	22.6	80	66	6.4
Ex. 12	0.11	4.2	109,600	212,200	4.5	19.0	87	68	6.6
Ex. 13	0.08	3.5	99,600	205,700	4.4	17.9	87	62	7.3
Ex. 14	No Flow	2.6	120,100	274,700	5.0	21.1	79	51	3.0

[00104] The data of Table 13 show that Examples 11, 12, 13 and 14 each have a a polydispersity index of ≤ 5.0.

[00105] The data of Table 13 show that Examples 11, 13, 14 had a melt temperature ≤ 87 °C.

[00106] The data of Table 13 show that Examples 11, 12, 13, and 14 had a melt index less than 0.5.

[00107] The data of Table 13 show that Examples 11, 12, 13, and 14 had a significantly positive MWCDI indicating broad orthogonal comonomer distribution and reverse comonomer distribution.

[00108] Deactivated Ge bridged Group IV metallocene (PPM) was determined using the calculated amount of polymer produced using ethylene and comonomer uptake, or consumption, divided by the amount (mass) of active Group IV catalyst used, and then multiplied by 1,000,000.

[00109] Productivity (grams polymer/grams total catalyst particle-hour) was determined as a ratio of calculated polymer produced, based upon ethylene and comonomer uptake, or consumption, to an amount of supported catalyst added to the reactor.

[00110] Efficiency (grams polymer/grams active catalyst metal) was determined as a ratio of polymer produced, based upon C2 and C6 uptake, or consumption, as a ratio to an amount of Group IV catalyst metal added to the reactor.

[00111] Melt index (I_2) was determined according to ASTM-1238, Condition B (190 °C, 2.16 kg).

[00112] Flow index (I_{21}) was determined according to ASTM-1238, Condition B (190 °C, 21.6 kg).

[00113] Melt temperature (Tm) was determined via Differential Scanning Calorimetry according to ASTM D 3418-08. In general, a scan rate of 10° C/min on a sample (10 mg) was used, and the second heating cycle was used to determine Tm.

[00114] Weight average molecular weight (Mw), number average molecular weight (Mn), Mp, and Polydispersity Index (Mw/Mn) were determined by GPC. Mp is reported as the molecular weight of the peak maxima.

[00115] GPC was determined as follows.

[00116] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 165 ºC and the column compartment was set at 155 ºC. The columns used were 4 TOSOH TSK GMHHR-H (30) HT 30-micron sized, mixed pore size columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00117] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 g/mol and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 ºC with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160 ºC for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

[00118] $$M_{polyethylene} = A \times \left(M_{polystyrene}\right)^{B} \quad \text{(EQ1)}$$

[00119] where M is the molecular weight, A has a value of 0.3992 and B is equal to 1.0.

[00120] A third order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[00121] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the

PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 12,000 for the 4 TOSOH TSK GMHHR-H (30) HT 30-micron sized, mixed pore size columns.

[00122] Samples were prepared in a semi-automatic manner with the PolymerChar Instrument Control Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 3 hours at 165 ºC under low speed shaking.

[00123] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCONE software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

[00124]
$$Mn_{(GPC)} = \frac{\sum_{i}^{i} IR_i}{\sum_{i}^{i} \left(IR_i / M_{polyethylene_i} \right)} \quad \text{(EQ 2)}$$

[00125]
$$Mw_{(GPC)} = \frac{\sum_{i}^{i} \left(IR_i * M_{polyethylene_i} \right)}{\sum_{i}^{i} IR_i} \quad \text{(EQ 3)}$$

[00126]
$$Mz_{(GPC)} = \frac{\sum_{i}^{i} \left(IR_i * M_{polyethylene_i}^{2} \right)}{\sum_{i}^{i} \left(IR_i * M_{polyethylene_i} \right)} \quad \text{(EQ 4)}$$

[00127] To monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate ($Flowrate_{(nominal)}$) for each sample by RV alignment of the respective decane peak within

the sample ($RV_{(FM\ Sample)}$) to that of the decane peak within the narrow standards calibration ($RV_{(FM\ Calibrated)}$). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate ($Flowrate_{(effective)}$) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCONE Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

[00128] Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample)) (EQ5).

[00129] IR5 GPC Octene Composition Calibration

[00130] A calibration for the IR5 detector rationing was performed using at least ten ethylene-based polymer standards (Octene as comonomer) made by single-site metallocene catalyst from a single reactor in solution process (polyethylene homopolymer and ethylene/octene copolymers) of a narrow SCB distribution and known comonomer content (as measured by ^{13}C NMR Method, Qiu et al., Anal. Chem.2009, 81, 8585–8589), ranging from homopolymer (0 SCB/1000 total C) to approximately 40 SCB/1000 total C, where total C = carbons in backbone + carbons in branches. Each standard had a weight-average molecular weight from 36,000 g/mole to 126,000 g/mole measured by GPC. Each standard had a molecular weight distribution (Mw/Mn) from 2.0 to 2.5. Polymer properties for the SCB standards are shown in Table A.

Table A: “Copolymer” Standards

Wt % Comonomer	IR5 Area ratio	SCB / 1000 Total C	Mw	Mw/Mn
23.1	0.2411	28.9	37,300	2.22
14.0	0.2152	17.5	36,000	2.19
0.0	0.1809	0.0	38,400	2.20
35.9	0.2708	44.9	42,200	2.18
5.4	0.1959	6.8	37,400	2.16
8.6	0.2043	10.8	36,800	2.20
39.2	0.2770	49.0	125,600	2.22
1.1	0.1810	1.4	107,000	2.09
14.3	0.2161	17.9	103,600	2.20
9.4	0.2031	11.8	103,200	2.26

[00131] The “IR5 Area Ratio (or “$IR5_{\ Methyl\ Channel\ Area}$ / $IR5_{\ Measurement\ Channel\ Area}$”)” of “the baseline-subtracted area response of the IR5 methyl channel sensor” to “the

baseline-subtracted area response of IR5 measurement channel sensor" (standard filters and filter wheel as supplied by PolymerChar: Part Number IR5_FWM01 included as part of the GPC-IR instrument) was calculated for each of the "Copolymer" standards. A linear fit of the Wt% Comonomer frequency versus the "IR5 Area Ratio" was constructed in the form of the following Equation 6:

$$\text{Wt\% Comonomer} = A_0 + [A_1 \times (\text{IR5}_{\text{Methyl Channel Area}} / \text{IR5}_{\text{Measurement Channel Area}})] \quad \text{(EQ 6)}$$

where A_0 is the "Wt% Comonomer" intercept at an "IR5 Area Ratio" of zero, and A_1 is the slope of the "Wt% Comonomer" versus "IR5 Area Ratio" and represents the increase in the Wt% Comonomer as a function of "IR5 Area Ratio." The IR5 area ratio is equal to the IR5 height ratio for narrow PDI and narrow SCBD standard materials.

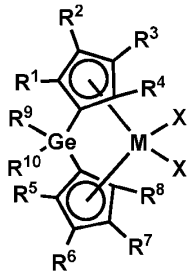
[00132] The comonomer distribution in an ethylene/α-olefin copolymer can be characterized as either normal (also referred to as having a Zeigler-Natta distribution), reverse, or flat. Several reported methods are utilized to quantify a Broad Orthogonal Composition Distribution (BOCD). Herein, a simple line fit is utilized such that the normal or reverse nature of the comonomer distribution can be quantified by the molecular weight comonomer distribution index (MWCDI), which is the slope of the linear regression of the comonomer distribution taken from a compositional GPC measurement, wherein the x-axis is Log(MW) and the y-axis is weight percent of comonomer. Short chain branching (SCB) was excluded from the MWCDI calculation according to the formula 0.1 > (SCBF)*(MW detector response) wherein SCBF is the SCB frequency measured in SCB/1000C. A reverse comonomer distribution is defined when the MWCDI > 0 and a normal comonomer distribution is defined when the MWCDI < 0. When the MWCDI = 0 the comonomer distribution is said to be flat. Additionally, the MWCDI quantifies the magnitude of the comonomer distribution. Comparing two polymers that have MWCDI > 0, the polymer with the greater MWCDI value is defined to have a greater, i.e., increased, BOCD; in other words, the polymer with the greater MWCDI value has a greater reverse comonomer distribution. Polymers with a relatively greater MWCDI, i.e., BOCD, can provide one or more improved physical properties, as compared to polymers having a relatively lesser MWCDI.

[00133] The comonomer content (C6 wt%), e.g., 1-hexene, incorporated in the polymers was determined by rapid FT-IR spectroscopy on the dissolved polymer in a GPC measurement. Comonomer content was determined with respect to polymer molecular weight by use of an infrared detector (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.

What is claimed is:

1. A polyolefin composition having from 50 to 99.9 wt % of units derived from ethylene based on a total weight of the polyolefin composition and from 1 to 50 wt% units derived from an α-olefin based on the total weight of the polyolefin composition, a weight average molecular weight from 30,000 to 400,000 g/mol, a melt temperature from 70 to 130 °C, a polydispersity index from 1.5 to 25.0, a melt index (I_2) from 0 to 1200 dg/min, a flow index (I_{21}) from 0.01 to 6000 dg/min, and from 0.0001 ppm to 10,000 ppm, based on the total weight of the polyolefin composition, of a deactivated Ge bridged Group IV metallocene represented by structure (I),



structure (I),

wherein R^1-R^4 are each independently hydrogen or a C1 to C8 alkyl, R^5-R^8 are each independently hydrogen or a C1 to C8 alkyl, R^9-R^{10} are each independently hydrogen, a C1 to C8 alkyl, or a C3 to C30 aryl or heteroaryl, M is a Group IV atom, and each X is independently a leaving group.

2. The polyolefin composition of claim 1, wherein the polyolefin composition has a reverse comonomer distribution.

3. The polyolefin composition of claim 1, wherein the polyolefin composition has a broad orthogonal comonomer or composition distribution as defined by a molecular weight comonomer distribution index > 0.

4. The polyolefin composition of any one of claims 1-3, wherein the α-olefin is 1-hexene.

5. The polyolefin composition of any one of claims 1-4, wherein 70 to 99 wt % of units derived from ethylene based on a total weight of the polyolefin composition and from 1 to 30 wt% units derived from an α-olefin based on the total weight of the polyolefin composition.

6. The polyolefin composition of any one of claims 1-5, wherein the polyolefin composition has a weight average molecular weight from 30,000 to 400,000 g/mol.

7. The polyolefin composition of any one of claims 1-6, wherein the polyolefin composition has a polydispersity index from 2 to 6 when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 110 °C and utilizing a H_2/C_2 ratio of 0 to 0.002, a C_6/C_2 ratio of 0 to 0.02, and an ethylene partial pressure up to 350 psi.

8. The polyolefin composition of any one of claims 1-7, wherein the polyolefin composition has a melt index (I_2) from 0 to 120 dg/min when made in a gas phase polymerization reactor having a reaction temperature of 80 °C to 110 °C and utilizing a H_2/C_2 ratio of 0 to 0.002, a C_6/C_2 ratio of 0 to 0.02, and an ethylene partial pressure of up to 350 psi.

10. The polyolefin composition of claim of any one of claims 1-9, wherein the polyolefin composition has a melt temperature from 70 to 130 °C when made in a gas phase polymerization reactor having a reaction temperature of 80 °C and utilizing a H_2/C_2 ratio of 0 to 0.002, a C_6/C_2 ratio of 0 to 0.02, and an ethylene partial pressure of up to 350 psi.

11. The polyolefin composition of any one of claims 1-10, wherein the deactivated Ge bridged Group IV metallocene represented by structure (I) is made by subjecting an activated Ge bridged Group IV metallocene represented by structure (I) to polymerization conditions to produce the polyolefin composition.