

HYDROCARBYL-MODIFIED METHYLALUMINOXANE COCATALYSTS FOR BIS-PHENYLPHENOXY METAL-LIGAND COMPLEXES

CROSS-REFERENCE

[0001] This application claims the benefit of U. S. Provisional Patent Application Serial No. 63/141,157 filed January 25, 2021, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to hydrocarbyl-modified methylaluminoxane activators for catalysts systems including bis-phenylphenoxy metal-ligand complexes.

BACKGROUND

[0003] Since the discovery of Ziegler and Natta on heterogeneous olefin polymerizations, global polyolefin production reached approximately 150 million tons per year in 2015, and it is rising due to increasing market demand. This success is based in part on a series of important breakthroughs in co-catalyst technology. The co-catalysts discovered include aluminoxanes, boranes, and borates with triphenylcarbenium or ammonium cations. These co-catalysts activate the homogeneous single-site olefin polymerization procatalysts, and polyolefins have been produced using these co-catalysts in industry.

[0004] As part of the catalyst composition in α -olefin polymerization reactions, the activator may have characteristics that are beneficial for the production of the α -olefin polymer and for final polymer compositions including the α -olefin polymer. Activator characteristics that increase the production of α -olefin polymers include, but are not limited to: rapid procatalyst activation, high catalyst efficiency, high temperature capability, consistent polymer composition, and selective deactivation.

[0005] Borate based co-catalysts in particular have contributed significantly to the fundamental understanding of olefin polymerization mechanisms, and have enhanced the ability for precise control over polyolefin microstructures by deliberately tuning catalyst structures and

processes. This results in stimulated interest in mechanistic studies and lead to the development of novel homogeneous olefin polymerization catalyst systems that have precise control over polyolefin microstructures and performance. However, once the cations of the activator or co-catalyst activate the procatalyst, the counter ion of the activator may remain in the polymer composition. As a result, the borate anions may affect the polymer composition. In particular, the size of the borate anion, the charge of the borate anion, the interaction of the borate anion with the surrounding medium, and the dissociation energy of the borate anion with available counterions will affect the ion's ability to diffuse through a surrounding medium such as a solvent, a gel, or a polymer material.

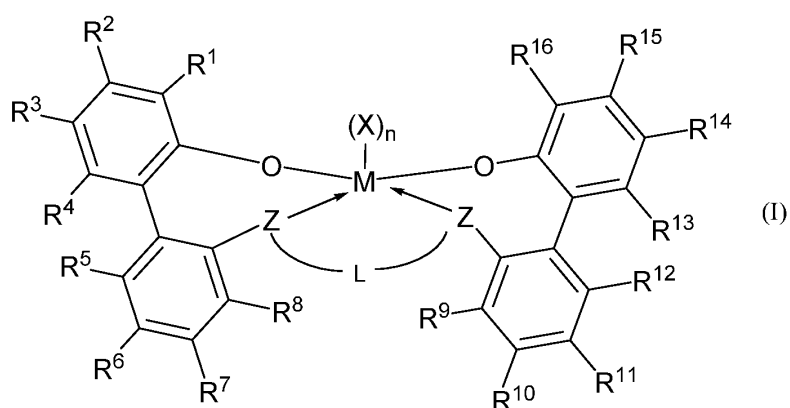
[0006] Modified methylaluminoxanes (MMAOs) can be described as a mixture of aluminoxane structures and trihydrocarbylaluminum species. Trihydrocarbylaluminum species, like trimethylaluminum are used as scavengers to remove impurities in the polymerization process which may contribute to the deactivation of the olefin polymerization catalyst. However, it is believed that trihydrocarbylaluminum species may be active in some polymerization systems. Catalyst inhibition has been noted when trimethylaluminum is present in propylene homopolymerizations with hafnocene catalysts at 60 °C (Busico, V. et. al. *Macromolecules* **2009**, *42*, 1789-1791). However, these observations convolute differences in MAO-activation versus borate activation, and even in direct comparison only possibly capture differences between some trimethylaluminum and none. Additionally, it is unclear that such observations extend to other catalysts systems, to ethylene polymerization, or to polymerizations conducted at higher temperatures. Regardless, the preference for soluble MAOs necessitates the use of MMAO and hence the presence of trihydrocarbylaluminum species.

[0007] Modified methylaluminoxanes (MMAO) are used as activators in some polyethylene processes in place of borate based activators. However, MMAO has been found to have negative impact on the performance of some catalysts, such as some bis-phenylphenoxy procatalysts, and have negatively impacted the production of polymer resins. The negative impact on the polymerization process includes decreasing catalyst activity, broadening composition distribution of the produced polymer, and negatively affecting the pellet handling.

SUMMARY

[0008] There is an ongoing need to create a catalyst system that does not include borate activators while maintaining catalyst efficiency, reactivity, and the ability to produce polymers with good physical properties, specifically a narrow composition distribution of the produced polymer

[0009] Embodiments of this disclosure includes processes of polymerizing olefin monomers. In one or more embodiments, the process includes reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system. The catalyst system includes hydrocarbyl-modified methylaluminoxane and one or more metal-ligand complexes. The metal-ligand complexes have a structure according to formula (I):

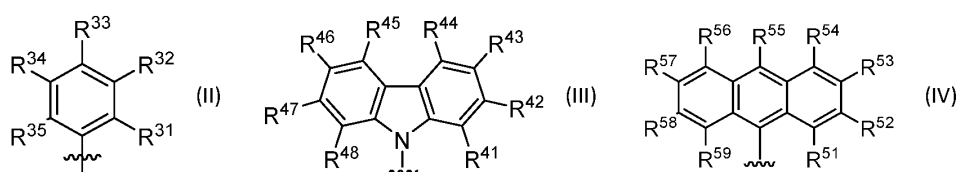


[0010] In formula (I), M is a metal selected from titanium, zirconium, or hafnium. The metal having a formal charge of +1, +2, or +3. Subscript n of $(X)_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated (C_2-C_{50}) hydrocarbon, unsaturated (C_2-C_{50}) heterohydrocarbon, saturated (C_2-C_{50}) heterohydrocarbon, (C_1-C_{50}) hydrocarbyl, (C_6-C_{50}) aryl, (C_6-C_{50}) heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4-C_{12}) diene, halogen, $-N(R^N)_2$, and $-N(R^N)COR^C$. The metal-ligand complex is overall charge-neutral. Each Z is independently chosen from $-O-$, $-S-$, $-N(R^N)-$, or $-P(R^P)-$. L is (C_1-C_{40}) hydrocarbylene or (C_2-C_{40}) heterohydrocarbylene.

[0011] In formula (I), R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently selected from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-Si(R^C)_3$,

$-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, and halogen.

[0012] In formula (I), R^1 and R^{16} are independently selected from the group consisting of $-\text{H}$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0013] In formulas (II), (III), and (IV), each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-\text{H}$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen.

[0014] In formulas (I), (II), (III), and (IV), each R^{C} , R^{P} , and R^{N} is independently a $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, or $-\text{H}$.

[0015] In some embodiments, the hydrocarbyl-modified methylaluminoxane has less than 50 mole percent trihydrocarbyl aluminum compound $\text{AlR}^{\text{A}}\text{R}^{\text{B}}\text{R}^{\text{C}}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A} , R^{B} , and R^{C} are independently $(\text{C}_1-\text{C}_{40})$ alkyl.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 is a Thermal Gradient Interaction Chromatograph (TGIC) with a chromatogram overlay for comparative examples, Entry 1 and Entry 2.

[0017] FIG. 2 is a Thermal Gradient Interaction Chromatograph (TGIC) with a chromatogram overlay for inventive example, Entry 3, and comparative example, Entry 4.

DETAILED DESCRIPTION

[0018] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0019] Common abbreviations are listed below:

[0020] **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn** : benzyl; ***i*-Pr** : *iso*-propyl; ***t*-Bu** : *tert*-butyl; ***t*-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf** : trifluoromethane sulfonate; **THF** : tetrahydrofuran; **Et₂O** : diethyl ether; **CH₂Cl₂** : dichloromethane; **CV** : column volume (used in column chromatography); **EtOAc** : ethyl acetate; **C₆D₆** : deuterated benzene or benzene-*d*₆; **CDCl₃** : deuterated chloroform; **Na₂SO₄** : sodium sulfate; **MgSO₄** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi** : *n*-butyllithium; ***t*-BuLi** : *tert*-butyllithium; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **GC** : gas chromatography; **LC** : liquid chromatography; **NMR** : nuclear magnetic resonance; **MS** : mass spectrometry; **mmol** : millimoles; **mL** : milliliters; **M** : molar; **min or mins** : minutes; **h or hrs** : hours; **d** : days.

[0021] The term “independently selected” is used herein to indicate that the R groups, such as, R¹, R², R³, R⁴, and R⁵, can be identical or different (e.g., R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc). A chemical name associated with an R group is intended to convey the chemical structure that is recognized in the art as corresponding to that of the chemical name. Thus, chemical names are intended to supplement and illustrate, not preclude, the structural definitions known to those of skill in the art.

[0022] The term “procatalyst” refers to a transition metal compound that has olefin polymerization catalytic activity when combined with an activator. The term “activator” refers to a compound that chemically reacts with a procatalyst in a manner that converts the procatalyst to a catalytically active catalyst. As used herein, the terms “co-catalyst” and “activator” are interchangeable terms.

[0023] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x-C_y)” means that the unsubstituted form of the

chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₅₀)alkyl is an alkyl group having from 1 to 50 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S. An R^S substituted chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–C₅₀)alkyl substituted with exactly one group R^S, where R^S is phenyl (–C₆H₅)” may contain from 7 to 56 carbon atoms. Thus, in general when a chemical group defined using the “(C_x–C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^S, the minimum and maximum total number of carbon atoms of the chemical group is determined by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^S.

[0024] The term “substitution” means that at least one hydrogen atom (–H) bonded to a carbon atom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g. R^S). The term “–H” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “–H” are interchangeable, and unless clearly specified have identical meanings.

[0025] The term “(C₁–C₅₀)alkyl” means a saturated straight or branched hydrocarbon radical containing from 1 to 50 carbon atoms; and the term “(C₁–C₃₀)alkyl” means a saturated straight or branched hydrocarbon radical of from 1 to 30 carbon atoms. Each (C₁–C₅₀)alkyl and (C₁–C₃₀)alkyl may be unsubstituted or substituted by one or more R^S. In some examples, each hydrogen atom in a hydrocarbon radical may be substituted with R^S, such as, for example trifluoromethyl. Examples of unsubstituted (C₁–C₅₀)alkyl are unsubstituted (C₁–C₂₀)alkyl; unsubstituted (C₁–C₁₀)alkyl; unsubstituted (C₁–C₅)alkyl; methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2-butyl; 2-methylpropyl; 1,1-dimethylethyl; 1-pentyl; 1-hexyl; 1-heptyl; 1-nonyl; and 1-decyl. Examples of substituted (C₁–C₄₀)alkyl are substituted (C₁–C₂₀)alkyl, substituted (C₁–C₁₀)alkyl, trifluoromethyl, and [C₄₅]alkyl. The term “[C₄₅]alkyl” means there is a maximum of 45 carbon atoms in the radical, including substituents, and is, for example, a (C₂₇–C₄₀)alkyl substituted by one R^S, which is a (C₁–C₅)alkyl, such as, for example, methyl, trifluoromethyl, ethyl, 1-propyl, 1-methylethyl, or 1,1-dimethylethyl.

[0026] The term (C₃–C₅₀)alkenyl means a branched or unbranched, cyclic or acyclic monovalent hydrocarbon radical containing from 3 to 50 carbon atoms, at least one double bond

and is unsubstituted or substituted by one or more R^S . Examples of unsubstituted (C_3 – C_{50})alkenyl: n-propenyl, isopropenyl, n-butenyl, isobutenyl, octenyl, decenyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, and cyclohexadienyl. Examples of substituted (C_3 – C_{50})alkenyl: (2-trifluoromethyl)pent-1-enyl, (3-methyl)hex-1-enyl, (3-methyl)hexa-1,4-dienyl and (Z)-1-(6-methylhept-3-en-1-yl)cyclohex-1-enyl.

[0027] The term “(C_3 – C_{50})cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S . Other cycloalkyl groups (e.g., (C_x – C_y)cycloalkyl) are defined in an analogous manner as having from x to y carbon atoms and being either unsubstituted or substituted with one or more R^S . Examples of unsubstituted (C_3 – C_{40})cycloalkyl are unsubstituted (C_3 – C_{20})cycloalkyl, unsubstituted (C_3 – C_{10})cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C_3 – C_{40})cycloalkyl are substituted (C_3 – C_{20})cycloalkyl, substituted (C_3 – C_{10})cycloalkyl, and 1-fluorocyclohexyl.

[0028] The term “halogen atom” or “halogen” means the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means anionic form of the halogen atom: fluoride (F^-), chloride (Cl^-), bromide (Br^-), or iodide (I^-).

[0029] The term “saturated” means lacking carbon–carbon double bonds, carbon–carbon triple bonds, and (in heteroatom-containing groups) carbon–nitrogen, carbon–phosphorous, and carbon–silicon double bonds. Where a saturated chemical group is substituted by one or more substituents R^S , one or more double or triple bonds optionally may be present in substituents R^S . The term “unsaturated” means containing one or more carbon–carbon double bonds or carbon–carbon triple bonds, or (in heteroatom-containing groups) one or more carbon–nitrogen double bonds, carbon–phosphorous double bonds, or carbon–silicon double bonds, not including double bonds that may be present in substituents R^S , if any, or in aromatic rings or heteroaromatic rings, if any.

[0030] The term “hydrocarbyl-modified methylaluminoxane” refers to a methylaluminoxane (MAO) structure comprising an amount of trihydrocarbyl aluminum. The hydrocarbyl-modified methylaluminoxane includes a combination of a hydrocarbyl-modified methylaluminoxane matrix and trihydrocarbyl aluminum. A total molar amount of aluminum in the hydrocarbyl-modified methylaluminoxane is composed of the aluminum contribution from the moles of

aluminum from the hydrocarbyl-modified methylaluminoxane matrix and moles of aluminum from the trihydrocarbyl aluminum. The hydrocarbyl-modified methylaluminoxane includes greater than 2.5 mole percent of trihydrocarbylaluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. These additional hydrocarbyl substituents can impact the subsequent aluminoxane structure and result in differences in the distribution and size of aluminoxane clusters (Bryliakov, K. P et. al. *Macromol. Chem. Phys.* **2006**, 207, 327-335). The additional hydrocarbyl substituents can also impart increased solubility of the aluminoxane in hydrocarbon solvents such as, but not limited to, hexane, heptane, methylcyclohexane, and ISOPAR E™ as demonstrated in US5777143. Modified methylaluminoxane compositions are generically disclosed and can be prepared as described in US5066631 and US5728855, both of which are incorporated herein by reference.

[0031] Embodiments of this disclosure includes processes of polymerizing olefin monomers. In one or more embodiments, the process includes reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system.

[0032] In some embodiments, the olefin monomer is (C₃–C₂₀) α -olefin. In other embodiments, the olefin monomer is not (C₃–C₂₀) α -olefin. In various embodiments, the olefin monomer is cyclic olefin.

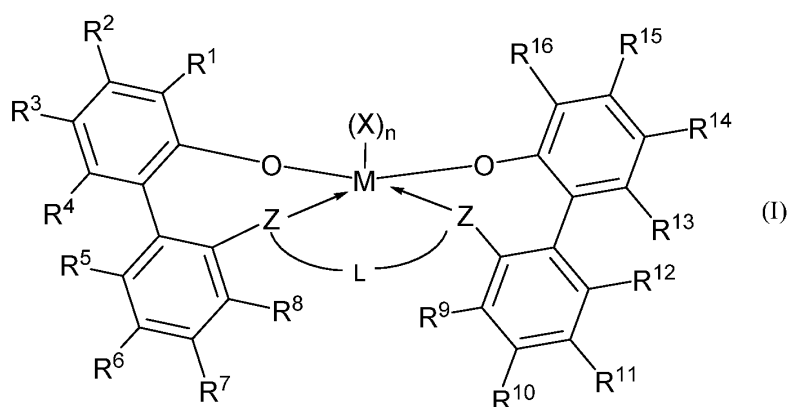
[0033] In one or more embodiments, the catalyst system includes hydrocarbyl-modified methylaluminoxane and a metal–ligand complex. The hydrocarbyl-modified methylaluminoxane having less than 50 mole percent trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. The trihydrocarbyl aluminum has a formula of AlR^{A1}R^{B1}R^{C1}, where R^{A1}, R^{B1}, and R^{C1} are independently (C₁–C₄₀)alkyl.

[0034] In embodiments, the hydrocarbyl-modified methylaluminoxane in the polymerization process has less than 30 mole percent and greater than 5 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. In some embodiments, the hydrocarbyl-modified methylaluminoxane has less than 25 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. In one or more embodiments, the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent or less than 10 mole percent of trihydrocarbyl aluminum based on

the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane. In various embodiments, the hydrocarbyl-modified methylaluminoxane is modified methylaluminoxane.

[0035] In some embodiments, the trihydrocarbyl aluminum has a formula of $\text{AlR}^{\text{A1}}\text{R}^{\text{B1}}\text{R}^{\text{C1}}$, where R^{A1} , R^{B1} , and R^{C1} are independently $(\text{C}_1\text{--}\text{C}_{10})$ alkyl. In one or more embodiments, R^{A1} , R^{B1} , and R^{C1} are independently methyl, ethyl, propyl, 2-propyl, butyl, *tert*-butyl, or octyl. In some embodiment, R^{A1} , R^{B1} , and R^{C1} are the same. In other embodiments, at least one of R^{A1} , R^{B1} , and R^{C1} is different from the other R^{A1} , R^{B1} , and R^{C1} .

[0036] In embodiments, the catalyst system includes hydrocarbyl-modified methylaluminoxane and a metal–ligand complex. In some embodiments, the catalyst system includes one or more metal–ligand complexes according to formula (I):

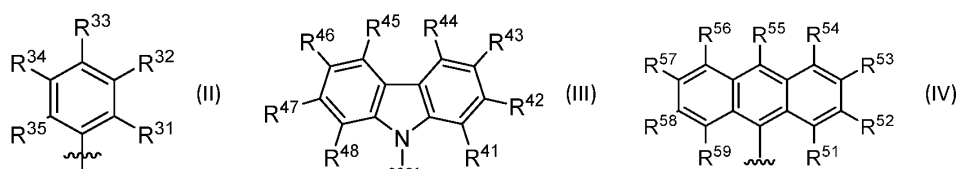


[0037] In formula (I), M is titanium, zirconium, hafnium, scandium, yttrium, or an element of the lanthanide series of the periodic table. In some embodiments, M is Zr or Sc.

[0038] Subscript n of $(\text{X})_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(\text{C}_2\text{--}\text{C}_{50})$ hydrocarbon, unsaturated $(\text{C}_2\text{--}\text{C}_{50})$ heterohydrocarbon, saturated $(\text{C}_2\text{--}\text{C}_{50})$ heterohydrocarbon, $(\text{C}_1\text{--}\text{C}_{50})$ hydrocarbyl, $(\text{C}_6\text{--}\text{C}_{50})$ aryl, $(\text{C}_6\text{--}\text{C}_{50})$ heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(\text{C}_4\text{--}\text{C}_{12})$ diene, halogen, $-\text{N}(\text{R}^{\text{N}})_2$, and $-\text{N}(\text{R}^{\text{N}})\text{COR}^{\text{C}}$. The metal–ligand complex is overall charge-neutral. Each Z is independently chosen from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^{\text{N}})-$, or $-\text{P}(\text{R}^{\text{P}})-$. L is $(\text{C}_1\text{--}\text{C}_{40})$ hydrocarbylene or $(\text{C}_2\text{--}\text{C}_{40})$ heterohydrocarbylene.

[0039] In formula (I), R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently selected from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^C\text{S}(\text{O})-$, $R^C\text{S}(\text{O})_2-$, $(R^C)_2\text{C}=\text{N}-$, $R^C\text{C}(\text{O})\text{O}-$, $R^C\text{OC}(\text{O})-$, $R^C\text{C}(\text{O})\text{N}(\text{R})-$, $(R^C)_2\text{NC}(\text{O})-$, and halogen.

[0040] In formula (I), R^1 and R^{16} are independently selected from the group consisting of $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^C\text{S}(\text{O})-$, $R^C\text{S}(\text{O})_2-$, $-\text{N}=\text{C}(R^C)_2$, $R^C\text{C}(\text{O})\text{O}-$, $R^C\text{OC}(\text{O})-$, $R^C\text{C}(\text{O})\text{N}(\text{R})-$, $(R^C)_2\text{NC}(\text{O})-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0041] In formulas (II), (III), and (IV), each of R^{31-35} , R^{41-48} , and R^{51-59} is independently chosen from $-H$, (C_1-C_{40}) hydrocarbyl, (C_1-C_{40}) heterohydrocarbyl, $-\text{Si}(R^C)_3$, $-\text{Ge}(R^C)_3$, $-\text{P}(R^P)_2$, $-\text{N}(R^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $R^C\text{S}(\text{O})-$, $R^C\text{S}(\text{O})_2-$, $(R^C)_2\text{C}=\text{N}-$, $R^C\text{C}(\text{O})\text{O}-$, $R^C\text{OC}(\text{O})-$, $R^C\text{C}(\text{O})\text{N}(R^N)-$, $(R^C)_2\text{NC}(\text{O})-$, or halogen.

[0042] In some embodiments, at least one of R^1 and R^{16} is a radical having formula (II), where R^{32} and R^{34} are *tert*-butyl. In one or more embodiments, R^{32} and R^{34} are (C_1-C_{12}) hydrocarbyl or $-\text{Si}[(C_1-C_{10})\text{alkyl}]_3$.

[0043] In some embodiments, when at least one of R^1 or R^{16} is a radical having formula (III), one of or both of R^{43} and R^{46} is *tert*-butyl and R^{41-42} , R^{44-45} , and R^{47-48} are $-H$. In other embodiments, one of or both of R^{42} and R^{47} is *tert*-butyl and R^{41} , R^{43-46} , and R^{48} are $-H$. In some embodiments, both R^{42} and R^{47} are $-H$. In various embodiments, R^{42} and R^{47} are (C_1-C_{20}) hydrocarbyl or $-\text{Si}[(C_1-C_{10})\text{alkyl}]_3$. In other embodiments, R^{43} and R^{46} are (C_1-C_{20}) hydrocarbyl or $-\text{Si}(C_1-C_{10})\text{alkyl}]_3$.

[0044] In embodiments, when at least one of R^1 or R^{16} is a radical having formula (IV), each R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} are $-H$, (C_1-C_{20}) hydrocarbyl, $-\text{Si}[(C_1-C_{20})\text{hydrocarbyl}]_3$, or $-\text{Ge}[(C_1-C_{20})\text{hydrocarbyl}]_3$. In some embodiments, at least one of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} is

(C₃–C₁₀)alkyl, –Si[(C₃–C₁₀)alkyl]₃, or –Ge[(C₃–C₁₀)alkyl]₃. In one or more embodiments, at least two of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ is a (C₃–C₁₀)alkyl, –Si[(C₃–C₁₀)alkyl]₃, or –Ge[(C₃–C₁₀)alkyl]₃. In various embodiments, at least three of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ is a (C₃–C₁₀)alkyl, –Si[(C₃–C₁₀)alkyl]₃, or –Ge[(C₃–C₁₀)alkyl]₃.

[0045] In some embodiments, when at least one of R¹ or R¹⁶ is a radical having formula (IV), at least two of R⁵², R⁵³, R⁵⁵, R⁵⁷, and R⁵⁸ are (C₁–C₂₀)hydrocarbyl or –C(H)₂Si[(C₁–C₂₀)hydrocarbyl]₃.

[0046] Examples of (C₃–C₁₀)alkyl include, but are not limited to: propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0047] In one or more embodiments, the metal–ligand complex of formula (I) is a procatalyst.

[0048] Examples of (C₃–C₁₀)alkyl include, but are not limited to: 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0049] In formula (I), R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ is independently selected from –H, (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, and halogen.

[0050] In one or more embodiments, R², R⁴, R⁵, R¹², R¹³, and R¹⁵ are hydrogen; and each Z is oxygen.

[0051] In various embodiments, at least one of R⁵, R⁶, R⁷, and R⁸ is a halogen atom; and at least one of R⁹, R¹⁰, R¹¹, and R¹² is a halogen atom. In some embodiments, R⁸ and R⁹ are independently (C₁–C₄)alkyl.

[0052] In some embodiments, R³ and R¹⁴ are (C₁–C₂₀)alkyl. In one or more embodiments, R³ and R¹⁴ are methyl and R⁶ and R¹¹ are halogen. In embodiments, R⁶ and R¹¹ are *tert*-butyl. In other embodiments, R³ and R¹⁴ are *tert*-octyl or *n*-octyl.

[0053] In various embodiments, R^3 and R^{14} are (C_1-C_{24}) alkyl. In one or more embodiments, R^3 and R^{14} are (C_4-C_{24}) alkyl. In some embodiments, R^3 and R^{14} are 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methyl-1-butyl, hexyl, 4-methyl-1-pentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl. In embodiments, R^3 and R^{14} are $-OR^C$, wherein R^C is (C_1-C_{20}) hydrocarbon, and in some embodiments, R^C is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl.

[0054] In one or more embodiments, one of R^8 and R^9 is not $-H$. In various embodiments, at least one of R^8 and R^9 is (C_1-C_{24}) alkyl. In some embodiments, both R^8 and R^9 are (C_1-C_{24}) alkyl. In some embodiments, R^8 and R^9 are methyl. In other embodiments, R^8 and R^9 are halogen.

[0055] In some embodiments, R^3 and R^{14} are methyl; In one or more embodiments, R^3 and R^{14} are (C_4-C_{24}) alkyl. In some embodiments, R^3 and R^{14} are 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methyl-1-butyl, hexyl, 4-methyl-1-pentyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0056] In various embodiments, in the metal-ligand complex of formula (I), R^6 and R^{11} are halogen. In some embodiments, R^6 and R^{11} are (C_1-C_{24}) alkyl. In various embodiments, R^6 and R^{11} independently are chosen from methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, *n*-pentyl, 3-methylbutyl, *n*-hexyl, 4-methylpentyl, *n*-heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl. In some embodiments, R^6 and R^{11} are *tert*-butyl. In embodiments, R^6 and R^{11} are $-OR^C$, wherein R^C is (C_1-C_{20}) hydrocarbyl, and in some embodiments, R^C is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl. In other embodiments, R^6 and R^{11} are $-SiR^C_3$, wherein each R^C is independently (C_1-C_{20}) hydrocarbyl, and in some embodiments, R^C is methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), or 1,1-dimethylethyl.

[0057] In some embodiments, any or all of the chemical groups (e.g., X and R^{1-59}) of the metal-ligand complex of formula (I) may be unsubstituted. In other embodiments, none, any, or all of the chemical groups X and R^{1-59} of the metal-ligand complex of formula (I) may be substituted with one or more than one R^S . When two or more than two R^S are bonded to a same chemical group of the metal-ligand complex of formula (I), the individual R^S of the chemical

group may be bonded to the same carbon atom or heteroatom or to different carbon atoms or heteroatoms. In some embodiments, none, any, or all of the chemical groups X and R¹⁻⁵⁹ may be persubstituted with R^S. In the chemical groups that are persubstituted with R^S, the individual R^S may all be the same or may be independently chosen. In one or more embodiments, R^S is chosen from (C₁-C₂₀)hydrocarbyl, (C₁-C₂₀)alkyl, (C₁-C₂₀)heterohydrocarbyl, or (C₁-C₂₀)heteroalkyl.

[0058] In formula (I), L is (C₁-C₄₀)hydrocarbylene or (C₁-C₄₀)heterohydrocarbylene; and each Z is independently chosen from -O-, -S-, -N(R^N)-, or -P(R^P)-. In one or more embodiments, L includes from 1 to 10 atoms.

[0059] In formulas (I), (II), (III), and (IV), each R^C, R^P, and R^N is independently a (C₁-C₃₀)hydrocarbyl, (C₁-C₃₀)heterohydrocarbyl, or -H.

[0060] In some embodiments of formula (I), the L may be chosen from (C₃-C₇)alkyl 1,3-diradicals, such as -CH₂CH₂CH₂-, -CH(CH₃)CH₂C*H(CH₃), -CH(CH₃)CH(CH₃)C*H(CH₃), -CH₂C(CH₃)₂CH₂-, cyclopentan-1,3-diyl, or cyclohexan-1,3-diyl, for example. In some embodiments, the L may be chosen from (C₄-C₁₀)alkyl 1,4-diradicals, such as -CH₂CH₂CH₂CH₂-, -CH₂C(CH₃)₂C(CH₃)₂CH₂-, cyclohexane-1,2-diyl dimethyl, and bicyclo[2.2.2]octane-2,3-diyl dimethyl, for example. In some embodiments, L may be chosen from (C₅-C₁₂)alkyl 1,5-diradicals, such as -CH₂CH₂CH₂CH₂CH₂-, and 1,3-bis(methylene)cyclohexane. In some embodiments, L may be chosen from (C₆-C₁₄)alkyl 1,6-diradicals, such as -CH₂CH₂CH₂CH₂CH₂CH₂- or 1,2-bis(ethylene)cyclohexane, for example.

[0061] In one or more embodiments, L is (C₂-C₄₀)heterohydrocarbylene. In some embodiments, L is -CH₂Ge(R^C)₂CH₂-, where each R^C is (C₁-C₃₀)hydrocarbyl. In some embodiments, L is -CH₂Ge(CH₃)₂CH₂-, -CH₂Ge(ethyl)₂CH₂-, -CH₂Ge(2-propyl)₂CH₂-, -CH₂Ge(*t*-butyl)₂CH₂-, -CH₂Ge(cyclopentyl)₂CH₂-, or -CH₂Ge(cyclohexyl)₂CH₂-.

[0062] In one or more embodiments, L is chosen from -CH₂-; -CH₂CH₂-; -CH₂(CH₂)_mCH₂-, CH₂(C(H)R^C)_mCH₂- and -CH₂(CR^C)_mCH₂-, where subscript m is from 1 to 3; -CH₂Si(R^C)₂CH₂-; -CH₂Ge(R^C)₂CH₂-; -CH(CH₃)CH₂CH*(CH₃); and -CH₂(phen-1,2-diyl)CH₂-; where each R^C in L is (C₁-C₂₀)hydrocarbyl.

[0063] Examples of such (C₁-C₁₂)alkyl include, but are not limited to methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl, cyclopentyl, or cyclohexyl, butyl, *tert*-butyl,

pentyl, hexyl, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpent-2-yl), nonyl, decyl, undecyl, and dodecyl.

[0064] In some embodiments, in the metal–ligand complex according to formula (I), both R^8 and R^9 are methyl. In other embodiments, one of R^8 and R^9 is methyl and the other of R^8 and R^9 is $-H$.

[0065] In the metal–ligand complex according to formula (I), X bonds with M through a covalent bond or an ionic bond. In some embodiments, X may be a monoanionic ligand having a net formal oxidation state of -1 . Each monoanionic ligand may independently be hydride, (C_1-C_{40}) hydrocarbyl carbanion, (C_1-C_{40}) heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, sulfate, $HC(O)O^-$, $HC(O)N(H)^-$, (C_1-C_{40}) hydrocarbyl $C(O)O^-$, (C_1-C_{40}) hydrocarbyl $C(O)N((C_1-C_{20})$ hydrocarbyl) $^-$, (C_1-C_{40}) hydrocarbyl $C(O)N(H)^-$, $R^K R^L B^-$, $R^K R^L N^-$, $R^K O^-$, $R^K S^-$, $R^K R^L P^-$, or $R^M R^K R^L Si^-$, where each R^K , R^L , and R^M independently is hydrogen, (C_1-C_{40}) hydrocarbyl, or (C_1-C_{40}) heterohydrocarbyl, or R^K and R^L are taken together to form a (C_2-C_{40}) hydrocarbylene or (C_1-C_{20}) heterohydrocarbylene and R^M is as defined above.

[0066] In some embodiments, X is a halogen, unsubstituted (C_1-C_{20}) hydrocarbyl, unsubstituted (C_1-C_{20}) hydrocarbyl $C(O)O^-$, or $R^K R^L N^-$, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{20}) hydrocarbyl. In some embodiments, each monodentate ligand X is a chlorine atom, (C_1-C_{10}) hydrocarbyl (e.g., (C_1-C_6) alkyl or benzyl), unsubstituted (C_1-C_{10}) hydrocarbyl $C(O)O^-$, or $R^K R^L N^-$, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{10}) hydrocarbyl.

[0067] In further embodiments, X is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. X is methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In one embodiment, n is 2 and at least two X independently are monoanionic monodentate ligands. In a specific embodiment, n is 2 and the two X groups join to form a bidentate ligand. In further embodiments, the bidentate ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0068] In one or more embodiments, each X is independently $-(CH_2)SiR^X_3$, in which each R^X is independently a (C_1-C_{30}) alkyl or a (C_1-C_{30}) heteroalkyl and at least one R^X is (C_1-C_{30}) alkyl. In some embodiments, when one of R^X is a (C_1-C_{30}) heteroalkyl, the heteroatom is silica or oxygen

atom. In some embodiments, R^X is methyl, ethyl, propyl, 2-propyl, butyl, 1,1-dimethylethyl (or *tert*-butyl), pentyl, hexyl, heptyl, n-octyl, *tert*-octyl, or nonyl.

[0069] In one or more embodiments X is $-(CH_2)Si(CH_3)_3$, $-(CH_2)Si(CH_3)_2(CH_2CH_3)$; $-(CH_2)Si(CH_3)(CH_2CH_3)_2$, $-(CH_2)Si(CH_2CH_3)_3$, $-(CH_2)Si(CH_3)_2(n\text{-butyl})$, $-(CH_2)Si(CH_3)_2(n\text{-hexyl})$, $-(CH_2)Si(CH_3)(n\text{-Oct})R^X$, $-(CH_2)Si(n\text{-Oct})R^X_2$, $-(CH_2)Si(CH_3)_2(2\text{-ethylhexyl})$, $-(CH_2)Si(CH_3)_2(dodecyl)$, $-CH_2Si(CH_3)_2CH_2Si(CH_3)_3$ (herein referred to as $-CH_2Si(CH_3)_2CH_2TMS$). Optionally, in some embodiments, the metal–ligand complex according to formula (I), exactly two R^X are covalently linked or exactly three R^X are covalently linked.

[0070] In some embodiments, X is $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$, $-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, in which subscript Q is 0, 1, 2 or 3 and each R^C is independently a substituted or unsubstituted (C_1-C_{30}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl.

Cocatalyst Component

[0071] The catalyst system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, the procatalyst according to a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Additionally, the metal–ligand complex according to formula (I) includes both a procatalyst form, which is neutral, and a catalytic form, which may be positively charged due to the loss of a monoanionic ligand, such as a methyl, benzyl or phenyl. Suitable activating co-catalysts for use herein include oligomeric alumoxanes or hydrocarbyl-modified methylaluminoxanes.

[0072] In embodiments, the catalyst system does not contain a borate activator. In one or more embodiments, the borate activator is tetrakis(pentafluorophenyl)borate(1 $^-$) anion and a countercation. In some embodiments, the borate activator is bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate.

Polyolefins

[0073] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene and propylene, to form ethylene-based polymers or propylene-based polymers. In some embodiments, there is only a single type of olefin or α -olefin in the polymerization scheme, creating a homopolymer. However, additional α -olefins may be incorporated into the polymerization procedure. The additional α -olefin co-monomers typically have no more than 20 carbon atoms. For example, the α -olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α -olefin co-monomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. For example, the one or more α -olefin co-monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene.

[0074] The ethylene-based polymers, for example homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins, may comprise from at least 50 mole percent (mol%) monomer units derived from ethylene. All individual values and subranges encompassed by "from at least 50 mole percent" are disclosed herein as separate embodiments; for example, the ethylene based polymers, homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins may comprise at least 60 mole percent monomer units derived from ethylene; at least 70 mole percent monomer units derived from ethylene; at least 80 mole percent monomer units derived from ethylene; or from 50 to 100 mole percent monomer units derived from ethylene; or from 80 to 100 mole percent monomer units derived from ethylene.

[0075] In some embodiments, the ethylene-based polymers may comprise at least 90 mole percent units derived from ethylene. All individual values and subranges from at least 90 mole percent are included herein and disclosed herein as separate embodiments. For example, the ethylene based polymers may comprise at least 93 mole percent units derived from ethylene; at least 96 mole percent units; at least 97 mole percent units derived from ethylene; or in the alternative, from 90 to 100 mole percent units derived from ethylene; from 90 to 99.5 mole percent units derived from ethylene; or from 97 to 99.5 mole percent units derived from ethylene.

[0076] In some embodiments of the ethylene-based polymer, the amount of additional α -olefin is less than 50 mol%; other embodiments include at least 1 mole percent (mol%) to 25 mol%; and in further embodiments the amount of additional α -olefin includes at least 5 mol% to 100 mol%.

[0077] Any conventional polymerization processes may be employed to produce the ethylene based polymers. Such conventional polymerization processes include, but are not limited to, solution polymerization processes, slurry phase polymerization processes, and combinations thereof using one or more conventional reactors such as loop reactors, isothermal reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[0078] In one embodiment, the ethylene-based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described herein, and optionally one or more co-catalysts. In another embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system in this disclosure, and as described herein, and optionally one or more other catalysts. The catalyst system, as described herein, can be used in the first reactor, or second reactor, optionally in combination with one or more other catalysts. In one embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described herein, in both reactors.

[0079] In another embodiment, the ethylene based polymer may be produced via solution polymerization in a single reactor system, for example a single loop reactor system, in which ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described within this disclosure, and optionally one or more co-catalysts, as described in the preceding paragraphs.

[0080] The ethylene based polymers may further comprise one or more additives. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers, and

combinations thereof. The ethylene based polymers may contain any amounts of additives. The ethylene based polymers may comprise from about 0 to about 10 percent by the combined weight of such additives, based on the weight of the ethylene based polymers and the one or more additives. The ethylene based polymers may further comprise fillers, which may include, but are not limited to, organic or inorganic fillers. The ethylene based polymers may contain from about 0 to about 20 weight percent fillers such as, for example, calcium carbonate, talc, or $\text{Mg}(\text{OH})_2$, based on the combined weight of the ethylene based polymers and all additives or fillers. The ethylene based polymers may further be blended with one or more polymers to form a blend.

[0081] In some embodiments, a polymerization process for producing an ethylene-based polymer may include polymerizing ethylene and at least one additional α -olefin in the presence of a catalyst system according to the present disclosure. The polymer resulting from such a catalyst system that incorporates the metal–ligand complex of formula (I) may have a density according to ASTM D792 (incorporated herein by reference in its entirety) from 0.850 g/cm³ to 0.970 g/cm³, from 0.880 g/cm³ to 0.920 g/cm³, from 0.880 g/cm³ to 0.910 g/cm³, or from 0.880 g/cm³ to 0.900 g/cm³, from 0.950 g/cm³ to 0.965 g/cm³ for example.

[0082] In another embodiment, the polymer resulting from the catalyst system according to the present disclosure has a melt flow ratio (I_{10}/I_2) from 5 to 15, where the melt index, I_2 , is measured according to ASTM D1238 (incorporated herein by reference in its entirety) at 190 °C and 2.16 kg load, and melt index I_{10} is measured according to ASTM D1238 at 190 °C and 10 kg load. In other embodiments the melt flow ratio (I_{10}/I_2) is from 5 to 10, and in others, the melt flow ratio is from 5 to 9.

[0083] In some embodiments, the polymer resulting from the catalyst system according to the present disclosure has a molecular-weight distribution (MWD) from 1 to 25, where MWD is defined as M_w/M_n with M_w being a weight-average molecular weight and M_n being a number-average molecular weight. In other embodiments, the polymers resulting from the catalyst system have a MWD from 1 to 6. Another embodiment includes a MWD from 1 to 3; and other embodiments include MWD from 1.5 to 2.5.

[0084] Embodiments of the catalyst systems described in this disclosure yield a catalyst system having a high efficiency in comparison to catalyst systems lacking the hydrocarbyl-modified methylaluminumoxane.

[0085] One or more features of the present disclosure are illustrated in view of the examples as follows:

EXAMPLES

[0086] **Procedure for Continuous Process Reactor Polymerization :** Raw materials (ethylene, 1-octene or 1-butene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked ISOPAR E commercially available from ExxonMobil Corporation) are purified with molecular sieves before introduction into the reaction environment. Hydrogen is supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized to above reaction pressure. The solvent and comonomer feed is pressurized to above reaction pressure. The individual catalyst components (metal ligand complex and cocatalysts) are manually batch diluted to specified component concentrations with purified solvent and pressured to above reaction pressure. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

[0087] The continuous solution polymerizations are carried out in a continuously stirred-tank reactor (CSTR). The combined solvent, monomer, comonomer and hydrogen feed to the reactor is temperature controlled between 5° C and 50° C and is typically 15-25° C. All of the components are fed to the polymerization reactor with the solvent feed. The catalyst is fed to the reactor to reach a specified conversion of ethylene. The cocatalyst component(s) is/are fed separately based on a calculated specified molar or ppm ratios. The effluent from the polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and polymer) exits the reactor and is contacted with water. In addition, various additives such as antioxidants, can be added at this point. The stream then goes through a static mixer to evenly disperse the mixture.

[0088] Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passes through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower-boiling components. The stream then passes through the reactor pressure control valve, across which the pressure is greatly reduced. From there, it enters a two stage separation system consisting of a devolatilizer and a vacuum extruder, where solvent and unreacted hydrogen, monomer, comonomer, and water are removed from the polymer. At the exit of the extruder, the strand of

molten polymer formed goes through a cold-water bath, where it solidifies. The strand is then fed through a strand chopper, where the polymer is cut it into pellets after being air-dried.

[0089] TEST METHODS

[0090] Unless otherwise indicated herein, the following analytical methods are used in describing aspects of the present disclosure:

[0091] Melt index

[0092] Melt indices I_2 (or I_2) and I_{10} (or I_{10}) of polymer samples were measured in accordance to ASTM D-1238 (method B) at 190 °C and at 2.16 kg and 10 kg load, respectively. Their values are reported in g/10 min.

[0093] Density

[0094] Samples for density measurement were prepared according to ASTM D4703. Measurements were made, according to ASTM D792, Method B, within one hour of sample pressing.

[0095] Gel Permeation Chromatography (GPC)

[0096] 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 160° Celsius and the column compartment was set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns and a 20-um pre-column. 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.

[0097] 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 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 dissolved at 80 degrees Celsius with gentle agitation 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)).:

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (\text{EQ 1})$$

where M is the molecular weight, A has a value of 0.4315 and B is equal to 1.0.

[0098] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points. A small adjustment to A (from approximately 0.375 to 0.445) was made to correct for column resolution and band-broadening effects such that linear homopolymer polyethylene standard is obtained at 120,000 Mw.

[0099] The total plate count of the GPC column set was performed with decane (prepared at 0.04 g in 50 milliliters of TCB and dissolved for 20 minutes with gentle agitation.) The plate count (Equation 2) and symmetry (Equation 3) were measured on a 200 microliter injection according to the following equations:

$$Plate\ Count = 5.54 * \left(\frac{(RV_{Peak\ Max})}{(Peak\ Width\ at\ \frac{1}{2}height)} \right)^2 \quad (\text{EQ 2})$$

where RV is the retention volume in milliliters, the peak width is in milliliters, the peak max is the maximum height of the peak, and $\frac{1}{2}$ height is $\frac{1}{2}$ height of the peak maximum.

$$Symmetry = \frac{(Rear\ Peak\ RV_{one\ tenth\ height} - RV_{Peak\ max})}{(RV_{Peak\ max} - Front\ Peak\ RV_{one\ tenth\ height})} \quad (\text{EQ 3})$$

where RV is the retention volume in milliliters and the peak width is in milliliters, Peak max is the maximum position of the peak, one tenth height is 1/10 height of the peak maximum, and where rear peak refers to the peak tail at later retention volumes than the peak max and where front peak refers to the peak front at earlier retention volumes than the peak max. The plate count for the chromatographic system should be greater than 18,000 and symmetry should be between 0.98 and 1.22.

[00100] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under “low speed” shaking.

[00101] 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 4-6, 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.

$$Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (EQ\ 4)$$

$$Mw_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ\ 5)$$

$$Mz_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (EQ\ 6)$$

[00102] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. To facilitate the highest accuracy of a RV measurement of the flow marker peak, a least-squares fitting routine is used to fit the peak of the flow marker concentration chromatogram to a quadratic equation. The first derivative of the quadratic equation is then used to solve for the true peak position. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 7. 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.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (\text{EQ 7})$$

High temperature thermal gradient interaction chromatography (HT-TGIC, or TGIC)

[00103] A commercial Crystallization Elution Fractionation instrument (CEF) (Polymer Char, Spain) was used to perform the high temperature thermal gradient interaction chromatography (HT-TGIC, or TGIC) measurement (Cong, et al., *Macromolecules*, 2011, 44 (8), 3062-3072.). The CEF instrument is equipped with an IR-5 detector. Graphite has been used as the stationary phase in an HT TGIC column (Freddy, A. Van Damme et al., US8, 476,076; Winniford et al., US 8,318,896.). A single graphite column (250 X 4.6 mm) was used for the separation. Graphite is packed into a column using a dry packing technique followed by a slurry packing technique (Cong et al., EP 2714226B1 and the reference cited). The experimental parameters were: top oven/transfer line/needle temperature at 150°C, dissolution temperature at 150°C, dissolution stirring setting of 2, pump stabilization time of 15 seconds, a pump flow rate for cleaning the column at 0.500 mL/min, pump flow rate of column loading at 0.300 ml/min, stabilization temperature at 150°C, stabilization time (pre-, prior to load to column) at 2.0 min, stabilization time (post-, after load to column) at 1.0 min, SF(Soluble Fraction) time at 5.0 min, cooling rate of 3.00°C/min from 150°C to 30°C, flow rate during cooling process of 0.04 ml/min, heating rate of 2.00°C/min from 30°C to 160°C, isothermal time at 160°C for 10 min, elution flow rate of 0.500 mL/min, and an injection loop size of 200 microliters.

[00104] The flow rate during cooling process was adjusted according to the length of graphite column such that all polymer fractions must remain on the column at the end of the cooling cycle.

[00105] Samples were prepared by the PolymerChar autosampler at 150°C, for 120 minutes, at a concentration of 4.0 mg/ml in ODCB (defined below). Silica gel 40 (particle size 0.2 ~0.5 mm, catalogue number 10181-3, EMD) was dried in a vacuum oven at 160°C, for about two hours, prior to use. For the CEF instrument equipped with an autosampler with N2 purging capability, Silica gel 40 is packed into three 300 x 7.5 mm GPC size stainless steel columns and the Silica gel 40 columns are installed at the inlet of the pump of the CEF instrument to purify ODCB; and no BHT is added to the mobile phase. ODCB dried with silica gel 40 is now referred to as

“ODCB.” The TGIC data was processed on a PolymerChar (Spain) “GPC One” software platform. The temperature calibration was performed with a mixture of about 4 to 6 mg Eicosane, 14.0 mg of isotactic homopolymer polypropylene iPP (polydispersity of 3.6 to 4.0, and molecular weight M_w reported as polyethylene equivalent of 150,000 to 190,000, and polydispersity (M_w/M_n) of 3.6 to 4.0, wherein the iPP DSC melting temperature was measured to be 158-159°C (DSC method described herein below). 14.0 mg of homopolymer polyethylene HDPE (zero comonomer content, weight average molecular weight (M_w) reported as polyethylene equivalent as 115,000 to 125,000, and polydispersity of 2.5 to 2.8), in a 10 mL vial filled with 7.0 mL of ODCB. The dissolution time was 2 hours at 160°C.

Data processing for polymer samples of HT-TGIC.

[00106] A solvent blank (pure solvent injection) was run at the same experimental conditions as the polymer samples. Data processing for polymer samples includes: subtraction of the solvent blank for each detector channel, temperature extrapolation as described in the calibration process, compensation of temperature with the delay volume determined from the calibration process, and adjustment in elution temperature axis to the 30°C and 160°C range as calculated from the heating rate of the calibration.

[00107] The chromatogram (measurement channel of the IR-5 detector) was integrated with PolymerChar “GPC One” software. A straight baseline was drawn from the visible difference, when the peak falls to a flat baseline (roughly a zero value in the blank subtracted chromatogram) at high elution temperature and the minimum or flat region of detector signal on the high temperature side of the soluble fraction (SF).

Broadness Indices of TGIC Profiles (B-Indices)

[00108] TGIC chromatogram is related to comonomer content and its distribution. It can be related to the number of catalyst active sites. TGIC profile can be affected by chromatographic related experimental factors at certain extent (Stregel, et al., “Modern size-exclusion liquid chromatography, Wiley, 2nd edition, Chapter 3). The TGIC broadness indices (B-Indices) can be used to make quantitative comparisons of the broadness of TGIC chromatogram of samples with different compositions and distributions. B-Indices can be calculated for any fraction of the maximum profile height. For example, the “N” B-Index can be obtained by measuring the profile width at $1/N^{\text{th}}$ of the profile’s maximum height and utilizing the follow equation:

$$B - \text{Index of TGIC profile (at } 1/N^{\text{th}} \text{ maximum height)} = \text{Profile width (at } \frac{1}{N^{\text{th}}} \text{ maximum height)} \times \frac{T_p}{150} \quad (\text{EQ. 8})$$

[00109] In Equation 8 (EQ. 8), T_p is the temperature where the maximum height is observed in the profile, where N is an integer 2, 3, 4, 5, 6, or 7. In cases where TGIC chromatograms have multiple peaks with similar peak heights, the peak at the highest elution temperature is defined as the profile temperature (T_p).

U-Index of TGIC profiles (U-Index)

[00110] TGIC was used to measure the composition distribution of polymers. To assess the uniformity of the composition distribution, the resulting chromatograms were fit to a Gaussian distribution according to the following equation:

$$f(x) = A_{max} * e^{-4\ln(2)\left(\frac{x-\mu}{\sigma}\right)^2} \quad (\text{EQ.9})$$

[00111] The fit was achieved by using a least-squares approach using the above function. The residual differences between the data and the function $f(x_i, \beta)$ were squared and subsequently summated, where x_i is the elution temperature above 35 °C where $i=0$, n is the at the final elution temperature of TGIC profile.

$$S = \sum_{i=0}^n (y_i - f(x_i, \beta))^2 \quad (\text{EQ. 10})$$

[00112] The fitted function was adjusted to provide a minimum value for the summation. In addition to the least squares method, the fitting equation was further combined with a weighting function to discourage over-estimation of peak shapes.

$$S = \sum_{i=0}^n w_i (y_i - f(x_i, \beta))^2 \quad (\text{EQ. 11})$$

[00113] Where w_i is equal to 1 for all positive instances of $(y_i - f(x_i, \beta))$ and is equal to 11 for all negative values of $(y_i - f(x_i, \beta))$. Using this method, the fitting function discourages overestimation of the peak shape and provides a better approximation of the area covered by a single site catalyst. Upon fitting the curve, the total area of the distribution covered by fit can be compared to the total

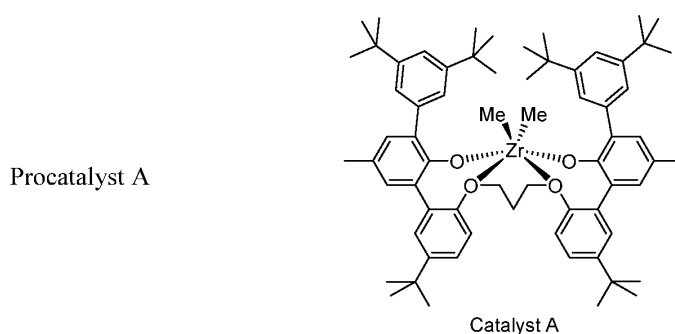
area of the sample chromatogram excluding the fraction remaining in 30 °C at the end of cooling step of TGIC experiment. Multiplication of this value by 100 gives us a uniformity index (U-index).

$$\text{U-index} = \left(\frac{\text{Area of Fit}}{\text{Area of Sample}} \right) \times 100 \quad (\text{EQ. 12})$$

[00114] As mentioned in the previous section, low density polymers generally broader molecular weight distribution (MWD) than high density polymers due the elution temperature. TGIC profile can be affected by polymer MWD(Abdulaal, et al., Macromolecular Chem Phy, 2017, 218, 1600332). Therefore, when analyzing the broadness of the MWD curve using TGIC, the breadth of the curve is not an accurate indication of the polymer chemical composition.

[00115] Example 1

[00116] The metal-complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of transition metal and a neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding transition metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. The techniques employed are the same as of analogous to those disclosed in United States Patent Nos. 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, US-A-2004/0220050.



[00117] Procatalysts A was polymerized in a continuous loop reactor using either borate, MMAO as the activator. The MMAO used for activation in these examples is an *n*-octyl modified aluminoxane. The methyl to octyl group substituents are present in roughly a 6 to 1 ratio and the sample contained roughly 15 % active aluminum as AIR3.

Table 1: Polymer Composition

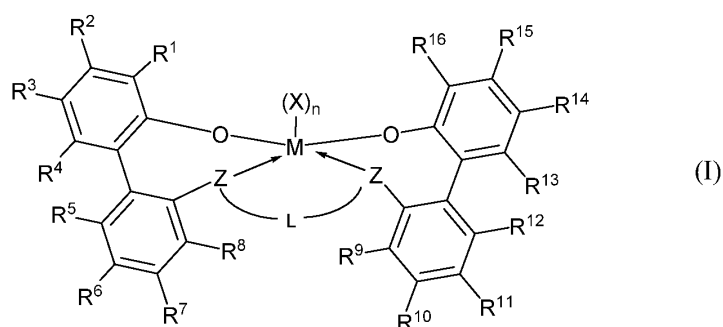
Entry	Comonomer	Purpose	Activator	Reactor Temp. (°C)	Density (g/cm ³)	Melt Index (dg/min)	4 B Index	5 B Index	U Index
1	1-octene	Comparative	MMAO	180	0.872	13.52	24.0	25.4	84.2
2	1-octene	Comparative	Borate	180	0.872	13.39	15.6	17.0	92.6
3	1-butene	Inventive	MMAO	185	0.8725	13.9	21.2	23.4	91.1
4	1-butene	Comparative	Borate	175	0.8734	13.7	29.9	58.3	92.7

[00118] The Thermal Gradient Interaction Chromatograph (TGIC) of Entry 1 and Entry 2, comparative examples, are shown in FIG. 1. Additionally, TGIC of Entry 3 was narrower than the TGIC of Entry 4. The shape of TGIC curves of Entries 1 to 4 provides the compositional distribution of the polymer produced in the polymerization reactions. When borate, as an activator, was added to the polymerization reaction, the compositional distribution of the produced polymer generally is narrower than the compositional distribution of the polymer produced when modified methylaluminoxane as an activator was added. However, the curve of the TGIC of Entry 3 is comparable to the narrowness of Entry 1.

[00119] The Thermal Gradient Interaction Chromatograph (TGIC) of Entry 1 and Entry 2, comparative examples, are shown in FIG. 1, while those of Entry 3 (Inventive) and Entry 4 (comparative) are shown in FIG. 2. The shape of TGIC curves of Entries 1 to 4 provides the compositional distribution of the polymer produced in the polymerization reactions. When comparing Entry 1 and Entry 2, both co-polymerized with 1-octene, FIG. 1 demonstrates that the borate-activated polymerization produces a narrower composition distribution than the MMAO-B-activated polymerization. However, comparing Entry 3 and Entry 4, both co-polymerized with 1-butene, FIG. 2 demonstrates that surprisingly the MMAO-B-activated polymerization produces a narrower and more desirable composition distribution than the borate-activated polymerization.

CLAIMS

1. A process of polymerizing olefin monomers, the process comprising reacting ethylene and 1-butene in the presence of a catalyst system, wherein the catalyst system comprises:
 hydrocarbyl-modified methylaluminoxane; and
 one or more metal–ligand complexes according to formula (I):



where:

M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from unsaturated

(C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, saturated

(C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl,

(C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl,

(C₄–C₁₂)diene, halogen, –N(R^N)₂, and –NCOR^C;

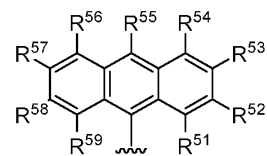
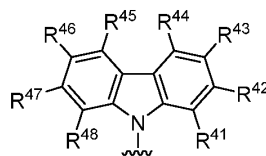
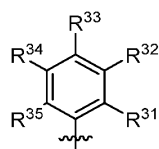
the metal–ligand complex is overall charge-neutral;

each Z is independently chosen from –O–, –S–, –N(R^N)–, or –P(R^P)–;

R¹ and R¹⁶ are independently selected from the group consisting of –H, (C₆–C₄₀)aryl,

(C₅–C₄₀)heteroaryl, radicals having formula (II), radicals having formula (III),

and radicals having formula (IV):



where each of R^{31–35}, R^{41–48}, and R^{51–59} is independently chosen from –H,

(C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂,

$-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$,
 $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen;
 R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently selected
 from $-\text{H}$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$,
 $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$,
 $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, and halogen;
 L is $(\text{C}_1-\text{C}_{40})$ hydrocarbylene or $(\text{C}_2-\text{C}_{40})$ heterohydrocarbylene; and
 each R^{C} , R^{P} , and R^{N} in formula (I) is independently a $(\text{C}_1-\text{C}_{30})$ hydrocarbyl,
 $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, or $-\text{H}$; and

wherein the catalysts system does not contain an activator containing boron.

2. The polymerization process according to claim 1, wherein hydrocarbyl-modified methylaluminoxane comprises less than 50 mole percent trihydrocarbyl aluminum compounds $\text{AlR}^{\text{A1}}\text{R}^{\text{B1}}\text{R}^{\text{C1}}$ based on the total moles of aluminum, where R^{A1} , R^{B1} , and R^{C1} are independently linear $(\text{C}_1-\text{C}_{40})$ alkyl, branched $(\text{C}_1-\text{C}_{40})$ alkyl, or $(\text{C}_6-\text{C}_{40})$ aryl
3. The polymerization process according to claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 30 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum.
4. The polymerization process according to claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 25 mole percent of trihydrocarbyl aluminum based on the total mole of hydrocarbyl-modified methylaluminoxane .
5. The polymerization process according to claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent of trihydrocarbyl aluminum based on the total mole of hydrocarbyl-modified methylaluminoxane.
6. The polymerization process according to any one of claim 1 to claim 4, where the hydrocarbyl-modified methylaluminoxane is modified methylaluminoxane.
7. The polymerization process according to any of the preceding claims, wherein:
 - at least one of R^5 , R^6 , R^7 , and R^8 is a halogen atom; and
 - at least one of R^9 , R^{10} , R^{11} , and R^{12} is a halogen atom.

8. The polymerization process according to any of claims 1 to 6, wherein R^8 and R^9 are independently (C_1-C_4) alkyl.
9. The polymerization process according to any of the preceding claims, wherein R^3 and R^{14} are (C_1-C_{20}) alkyl.
10. The polymerization process according to any one of the preceding claims, wherein R^3 and R^{14} are methyl, R^6 and R^{11} are halogen.
11. The polymerization process according to any one of claims 1-7, wherein R^6 and R^{11} are *tert*-butyl.
12. The polymerization process according to any one of claims 1 to 7, wherein R^3 and R^{14} are methyl, *tert*-octyl or *n*-octyl.
13. The polymerization process according to any one of the preceding claims, wherein M is Zr.
14. The polymerization process according to any one of the preceding claims, wherein L is chosen from $-CH_2(CH_2)_mCH_2-$, where m is 1 to 3, $-CH_2Si(R^C)(R^D)CH_2-$, $-CH_2Ge(R^C)(R^D)CH_2-$, $-CH(CH_3)CH_2CH(CH_3)-$, bis(methylene)cyclohexan-1,2-diyl; $-CH_2CH(R^C)CH_2-$, $-CH_2C(R^C)_2CH_2-$, where each R^C in L is (C_1-C_{20}) hydrocarbyl and R^D in L is (C_1-C_{20}) hydrocarbyl.
15. The polymerization process according to any one of the preceding claims, wherein at least one of R^1 and R^{16} is a radical having formula (II).
16. The polymerization process according to claim 15, wherein R^{32} and R^{34} are (C_1-C_{12}) hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.
17. The polymerization process according to any one of claims 1 to 14, wherein at least one of R^1 and R^{16} is a radical having formula (IV).
18. The polymerization process according to claim 17, wherein at least two of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} are (C_1-C_{20}) hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

19. The polymerization process according to any one of the preceding claims, wherein the polymerization process is a solution polymerization reaction.