

MULTIMODAL POLYMERIZATION PROCESSES WITH MULTI-CATALYST SYSTEMS
CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/594,830 filed October 31, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to olefin polymerization catalyst systems and processes, and, more specifically, to the olefin polymerization catalyst systems including one or more bis(biphenylphenoxy) procatalysts and one or more guanidine procatalysts and polymerization processes incorporating the catalyst systems to produce bimodal polymers.

BACKGROUND

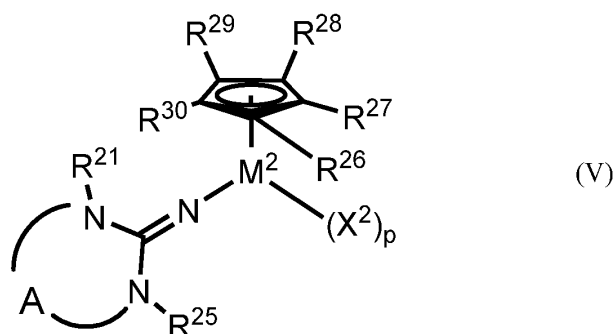
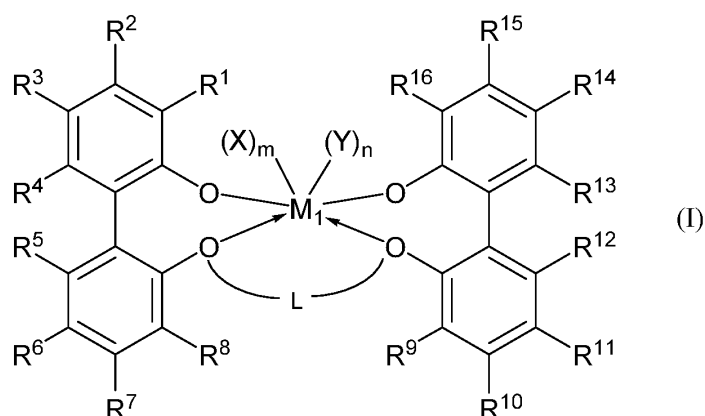
[0003] Olefin-based polymers such as polyethylene, ethylene-based polymers, polypropylene, and propylene-based polymers are produced via various catalyst systems. Selection of such catalyst systems used in the polymerization process of the olefin-based polymers is an important factor contributing to the characteristics and properties of such olefin-based polymers. Despite the research efforts in developing catalyst systems suitable for olefin polymerization, such as polyethylene or polypropylene polymerization, there is still a need to increase the efficiencies of catalyst systems that are capable of producing polymers with differentiated polymer molecular weights.

SUMMARY

[0004] Embodiments of the present disclosure meet this need by combining catalysts derived from two different classes – bis(biphenylphenoxy) metal–ligand complexes (BPP catalysts) and guanidine complexes (GD catalysts).

[0005] Without being limited by theory, the weight average molecular weight of the polymer produced by GD catalysts is much more sensitive to hydrogen than is the molecular weight of the polymer produced by BPP catalysts. Consequently, the molecular weight split (difference in molecular weight of the polyethylene produced by the two catalysts) can be tailored by adjusting hydrogen levels without significantly changing other conditions. The small changes in the hydrogen level, such as changes of 5 mmol, results in large differences in molecular weight of the polymer produced by the GD catalyst. Comparatively, the same increases in H₂ lead to smaller changes in the polymer produced by the BPP catalyst. FIGS. 1A, 1B, and 1C illustrate the changes in molecular weight of the polyethylene produced by the BPP catalysts and the GD catalysts.

[0006] Embodiments of this disclosure include process of producing ethylene-based polymers, the process comprising reacting ethylene and optionally one or more olefin monomers in one or more reactors in the presence of a catalyst system and optionally in the presence of hydrogen; the catalyst system being comprised of two or more catalysts, at least one of which is derived from bis(biphenylphenoxy) procatalysts according to formula (I) and at least one of which is derived from guanidine procatalysts according to formula (V) as detailed below.



BRIEF DESCRIPTION OF FIGURES

[0007] FIG. 1A shows two theoretical molecular weight distribution curves of two unimodal polymer compositions produced by a BPP and produced by a guanidine catalyst with no hydrogen gas in the reactor chamber.

[0008] FIG. 1B shows two theoretical molecular weight distribution curves of two unimodal polymer compositions produced by a BPP and produced by a guanidine catalyst with 5-10 mmol of hydrogen gas in the reactor chamber.

[0009] FIG. 1C shows two theoretical molecular weight distribution curves of two unimodal polymer compositions produced by a BPP and produced by a guanidine catalyst with 20-40 mmol hydrogen gas in the reactor chamber.

[0010] FIG. 2 is a molecular weight distribution curve of bimodal polymer compositions produced by a BPP-1 and a GD-1 with varying amounts of hydrogen gas in the reactor chamber. These amounts of hydrogen gas are 5 mmol, 20 mmol, and 40 mmol.

[0011] FIG. 3 is a molecular weight distribution curve of bimodal polymer compositions produced by a BPP-2 and a GD-1 with varying amounts of hydrogen gas in the reactor chamber. These amounts of hydrogen gas are 5 mmol, 20 mmol, and 40 mmol.

[0012] FIG. 4 is a molecular weight distribution curve of bimodal polymer compositions produced by a BPP-1 and a GD-2 with varying amounts of hydrogen gas in the reactor chamber. These amounts of hydrogen gas are 5 mmol, 20 mmol, and 40 mmol.

[0013] FIG. 5 is a molecular weight distribution curve of bimodal polymer compositions produced by a BPP-1 and a GD-3 with varying amounts of hydrogen gas in the reactor chamber. These amounts of hydrogen gas are 5 mmol, 20 mmol, and 40 mmol.

DETAILED DESCRIPTION

[0014] Specific embodiments of catalyst systems will 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.

[0015] Common abbreviations are listed below:

[0016] **R, Z, M, X and n**: as defined above; **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**: butyllithium; ***t*-BuLi**: *tert*-butyllithium; **Cu₂O**: Copper (I) Oxide; ***N,N'*-DMEDA**: *N,N'*-dimethylethylenediamine; **K₃PO₄**: Potassium phosphate tribasic; **Pd(AmPhos)Cl₂**: Bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II); **PdCl(crotyl)Amphos**: Chloro(crotyl)[di-*tert*-butyl(4-dimethylaminophenyl)phosphine]palladium(II); **Pd(dppf)Cl₂**: [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride; **AgNO₃**: Silver nitrate; **K₂CO₃**: potassium carbonate; **Cs₂CO₃**: cesium carbonate; ***i*-PrOBPin**: 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; **BrCl₂CCl₂Br**: 1,2-dibromotetrachloroethane; **N₂**: nitrogen gas; **PhMe**:

toluene; **PPR** : parallel pressure reactor; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **GC** : gas chromatography; **GPC** : gel permeation 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; **R_f** : retention fraction; **TLC** : thin-layered chromatography; **rpm** : revolution per minute; **LogM** : the log of the molecular weight; **dWf** : the change in the weight fraction; **dLogM** : the change in the log of the molecular weight; **Mw** : weight average molecular weight; **Mn** : number average molecular weight; **Mz** : z-average molar mass.

[0017] The term “independently selected” followed by multiple options is used herein to indicate that individual R groups appearing before the term, such as R¹, R², R³, R⁴, and R⁵, can be identical or different, without dependency on the identity of any other group also appearing before the term.

[0018] The term “procatalyst” refers to a compound that has catalytic activity when combined with an activator. The term “activator” refers to a compound that chemically reacts with a procatalyst in a manner that converts the procatalyst to a catalytically active catalyst. As used herein, the terms “co-catalyst” and “activator” are interchangeable terms.

[0019] 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 version of a chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–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.

[0020] The term “substitution” means that at least one hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g. R^S). The term “persubstitution” means that every hydrogen atom (H) bonded

to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). The term “polysubstitution” means that at least two, but fewer than all, hydrogen atoms bonded to carbon atoms or heteroatoms of a corresponding unsubstituted compound or functional group are replaced by a substituent. 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.

[0021] The terms “halogen atom,” “halogen,” “halide,” “saturated,” “unsaturated,” ““(C₁-C₅₀)hydrocarbyl,” ““(C₁-C₅₀)alkyl,” ““(C₁-C₁₈)alkyl,” ““(C₆-C₅₀)aryl,” ““(C₃-C₅₀)cycloalkyl,” ““(C₁-C₅₀)alkylene,” “heteroatom,” and ““(C₁-C₅₀)heteroalkyl” are as defined in publication number WO2020185494A1.

[0022] The term “polymer” refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term “homopolymer,” usually employed to refer to polymers prepared from only one type of monomer as well as “copolymer” which refers to polymers prepared from two or more different monomers.

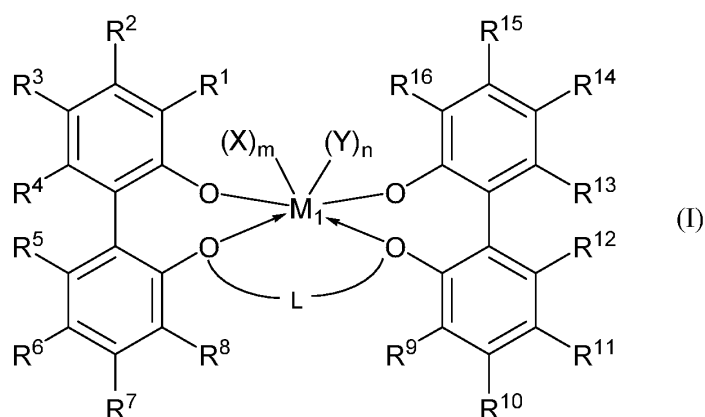
[0023] “Polyethylene” or “ethylene-based polymer” shall mean polymers comprising greater than 50% by weight of units which have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more comonomers). Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE); Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); single-site catalyzed Linear Low Density Polyethylene, including both linear and substantially linear low density resins (m-LLDPE); Medium Density Polyethylene (MDPE); and High Density Polyethylene (HDPE).

[0024] As used herein, “multimodal” refers to polymers produced from a plurality of polymer fractions, each polymer fraction being produced by a distinct catalyst. Multimodal may include bimodal polymers having two polymer fractions, trimodal ethylene-based polymers having three polymer fractions, or polymers having more than three polymer fractions.

[0025] Embodiments of this disclosure include process of producing ethylene-based polymers, the process comprising reacting ethylene and optionally one or more olefin monomers in one or more reactors in the presence of a catalyst system and optionally in the presence of hydrogen.

[0026] The catalyst system includes one or more bis(biphenylphenoxy) procatalysts according to formula (I) and one or more guanidine procatalysts according to formula (V).

[0027] Embodiments of this disclosure include catalyst systems that include one or more bis(biphenylphenoxy) procatalysts according to formula (I):



[0028] In formula (I), M_1 is titanium, zirconium, hafnium, scandium, or yttrium; m is 1 or 2; n is 0, 1, or 2; and each X is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$, $-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, $-CH_2Ge(R^C)_{3-Q}(OR^C)_Q$, $-Ge(R^C)_{3-Q}(OR^C)_Q$, $-P(R^C)_{2-W}(OR^C)_W$, $-P(O)(R^C)_{2-W}(OR^C)_W$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^C Si(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$, $-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$, $-NHC(O)R^C$, $-C(O)N(R^C)_2$, $-C(O)NHR^C$, $-C(O)NH_2$, a halogen, $B(R^Y)_4$, $Al(R^Y)_4$, or $Ga(R^Y)_4$, or a hydrogen, wherein each R^C is independently a (C_1-C_{30}) hydrocarbyl, or (C_1-C_{30}) heterohydrocarbyl, and each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^Y is $-H$, (C_1-C_{30}) hydrocarbyl, or halogen atom, wherein an X ligand and a Y ligand can be connected to form a ring. The metal-ligand complex is overall charge-neutral.

[0029] In the metal-ligand complex according to formula (I), each Y bonds with M_1 through a dative bond or an ionic bond. In one or more embodiments, Y is a Lewis base. The Lewis base may be a compound or an ionic species, which can donate an electron pair to an acceptor compound. For purposes of this description, the acceptor compound is M_1 , the metal of the metal-ligand complex of formula (I). The Lewis base may be neutral or anionic. In some embodiments, the Lewis base may be a heterohydrocarbon or an unsaturated hydrocarbon. Examples of neutral heterohydrocarbon Lewis bases includes, but are not limited to, amines,

trialkylamines, ethers, cycloethers, or sulfides. An example of anionic hydrocarbon includes, but is not limited to, cyclopentadienyl. An example of a neutral hydrocarbon Lewis Base includes, but is not limited to, 1,3-buta-di-ene.

[0030] In some embodiments, the Lewis base is (C₁–C₂₀)hydrocarbon. In some embodiments, the Lewis base is cyclopentadiene or 1,3-buta-di-ene. In various embodiments, the Lewis base is (C₁–C₂₀)heterohydrocarbon, wherein the hetero atom of the heterohydrocarbon is oxygen. In some embodiments, Y is tetrahydrofuran, diethyl ether, or methyl *tert*-butyl ether (MTBE).

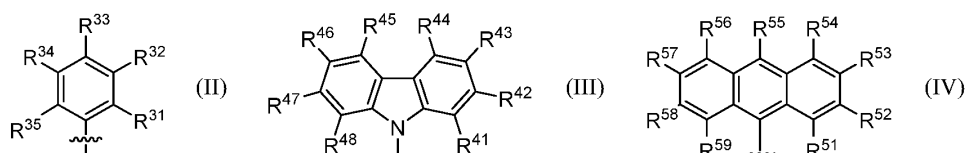
[0031] Additionally, each X and each Y can be a monodentate ligand that, independently from any other ligands X and Y, is a halogen, unsubstituted (C₁–C₂₀)hydrocarbonyl, unsubstituted (C₁–C₂₀)hydrocarbonylC(O)O–, or R^KR^LN–, wherein each of R^K and R^L independently is an unsubstituted(C₁–C₂₀)hydrocarbonyl. In some embodiments, each monodentate ligand X is a chlorine atom, (C₁–C₁₀)hydrocarbonyl (e.g., (C₁–C₆)alkyl or benzyl), unsubstituted (C₁–C₁₀)hydrocarbonylC(O)O–, or R^KR^LN–, wherein each of R^K and R^L independently is an unsubstituted (C₁–C₁₀)hydrocarbonyl. In one or more embodiments of formula (I), X is benzyl, chloro, –CH₂SiMe₃, or phenyl.

[0032] In further embodiments, each X and/or each Y is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments, each X is the same. In other embodiments, at least two X are different from each other. In the embodiments in which at least two X are different from at least one X, X is a different one of methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In further embodiments, the bidentate ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0033] In some embodiments, any or all of the chemical groups (e.g., X, Y and R¹–R¹⁶) of the metal–ligand complex of formula (I) may be unsubstituted. In other embodiments, none, any, or all of the chemical groups X and R¹–R¹⁶ 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–R¹⁶ 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.

[0034] In formula (I), L is (C₁–C₄₀)hydrocarbylene or (C₂–C₄₀)heterohydrocarbylene. In one or more embodiments, L is chosen from –CH₂(CH₂)_mCH₂–, –CH₂Si(R^C)(R^D)CH₂–, –CH₂Ge(R^C)(R^D)CH₂–, –CH₂(CH₃)CH₂CH*(CH₃), bis(methylene)cyclohexan-1,2-diyl; –CH₂CH(R^C)CH₂–, –CH₂C(R^C)₂CH₂–, where each R^C in L is (C₁–C₂₀)hydrocarbyl and R^D in L is (C₁–C₂₀)hydrocarbyl.

[0035] R¹ and R¹⁶ are independently selected from the group consisting of –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–, –N=C(R^C)₂, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, 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, –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^N)–, (R^C)₂NC(O)–, or halogen.

[0036] The groups R¹ and R¹⁶ in the metal–ligand complex of formula (I) are chosen independently of one another. For example, R¹ may be chosen from a radical having formula (II), (III), or (IV) and R¹⁶ may be a (C₁–C₄₀)hydrocarbyl; or R¹ may be chosen from a radical having formula (II), (III), or (IV) and R¹⁶ may be chosen from a radical having formula (II), (III), or (IV) the same as or different from that of R¹. Both R¹ and R¹⁶ may be radicals having formula (II), for which the groups R^{31–35} are the same or different in R¹ and R¹⁶. In other examples, both R¹ and R¹⁶ may be radicals having formula (III), for which the groups R^{41–48} are the same or different in R¹ and R¹⁶, or both R¹ and R¹⁶ may be radicals having formula (IV), for which the groups R^{51–59} are the same or different in R¹ and R¹⁶.

[0037] In some embodiments, at least one of R¹ and R¹⁶ is a radical having formula (II), where R³² and R³⁴ are *tert*-butyl. In one or more embodiments, R³² and R³⁴ are (C₁–C₁₂)hydrocarbyl or –Si[(C₁–C₁₀)alkyl]₃.

[0038] In some embodiments, when at least one of R¹ or R¹⁶ is a radical having formula (III), one of or both of R⁴³ and R⁴⁶ 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 $-Si[(C_1-C_{10})alkyl]_3$. In other embodiments, R^{43} and R^{46} are (C_1-C_{20}) hydrocarbyl or $-Si(C_1-C_{10})alkyl]_3$. In some embodiments, R^{42} and R^{43} are linked to form a cyclic structure, and R^{46} and R^{47} are linked to form a cyclic structure.

[0039] 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, $-Si[(C_1-C_{20})hydrocarbyl]_3$, or $-Ge[(C_1-C_{20})hydrocarbyl]_3$. In some embodiments, at least one of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} is $(C_3-C_{10})alkyl$, $-Si[(C_3-C_{10})alkyl]_3$, or $-Ge[(C_3-C_{10})alkyl]_3$. In one or more embodiments, at least two of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} is a $(C_3-C_{10})alkyl$, $-Si[(C_3-C_{10})alkyl]_3$, or $-Ge[(C_3-C_{10})alkyl]_3$. In various embodiments, at least three of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} is a $(C_3-C_{10})alkyl$, $-Si[(C_3-C_{10})alkyl]_3$, or $-Ge[(C_3-C_{10})alkyl]_3$.

[0040] In some embodiments, when at least one of R^1 or R^{16} is a radical having formula (IV), at least two of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} are (C_1-C_{20}) hydrocarbyl or $-C(H)_2Si[(C_1-C_{20})hydrocarbyl]_3$.

[0041] Examples of $(C_3-C_{10})alkyl$ 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.

[0042] In some embodiment of the metal–ligand catalyst according to formula (I), R^1 and R^{16} are chosen from 3,5-di-*tert*-butylphenyl; 2,4,6-trimethylphenyl; 2,4,6-triisopropylphenyl; 3,5-diisopropylphenyl; carbazolyl; carbazol-9-yl, 1,2,3,4-tetrahydrocarbazolyl; 1,2,3,4,5,6,7,8-octahydrocarbazolyl; 3,6-bis-(3,5-di-*tert*-butylphenyl)carbazol-9-yl; 3,6-bis-(2,4,6-trimethylphenyl)carbazol-9-yl; 3,6-bis-(2,4,6-triisopropylphenyl)carbazol-9-yl; 2,7-di(tertiarybutyl)-carbazol-9-yl; 2,7-di(tertiary-octyl)-carbazol-9-yl; 2,7-diphenylcarbazol-9-yl; 2,7-bis(2,4,6-trimethylphenyl)-carbazol-9-yl anthracenyl; 1,2,3,4-tetrahydroanthracenyl; 1,2,3,4,5,6,7,8-octahydroanthracenyl; phenanthrenyl; 1,2,3,4,5,6,7,8-octahydrophenanthrenyl; 1,2,3,4-tetrahydronaphthyl; 2,6-dimethylphenyl; 2,6-diisopropylphenyl; 3,5-diphenylphenyl; 1-naphthyl; 2-methyl-1-naphthyl; 2-naphthyl; 1,2,3,4-tetrahydronaphth-5-yl; 1,2,3,4-tetrahydronaphth-6-yl; anthracen-9-yl; 1,2,3,4-tetrahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydrophenanthren-9-yl; indolyl; indolinyl; quinolinyl; 1,2,3,4-tetrahydroquinolinyl; isoquinolinyl; or 1,2,3,4-tetrahydroisoquinolinyl.

[0043] 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, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen. Each R^C , R^P , and R^N in formula (I) is independently a (C_1-C_{30}) hydrocarbyl, (C_1-C_{30}) heterohydrocarbyl, or $-H$.

[0044] 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.

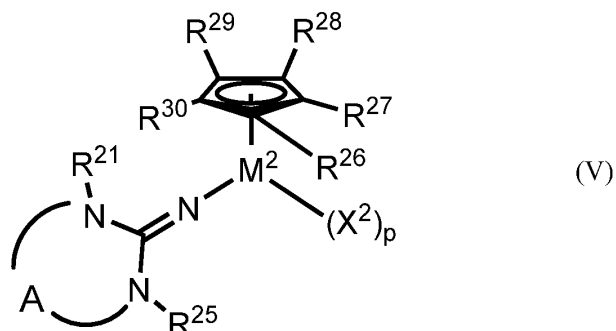
[0045] In one or more embodiments, one of R^8 and R^9 is not $-H$. In various embodiments, at least one of R^8 and R^9 is (C_1-C_{24}) alkyl. In some embodiments, both R^8 and R^9 are (C_1-C_{24}) alkyl. In some embodiments, R^8 and R^9 are methyl. In other embodiments, R^8 and R^9 are halogen.

[0046] 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^8 and R^9 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.

[0047] 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, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, 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.

[0048] 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 $-H$.

[0049] Embodiments of this disclosure include catalyst systems that include one or more guanidine procatalysts according to formula (V):



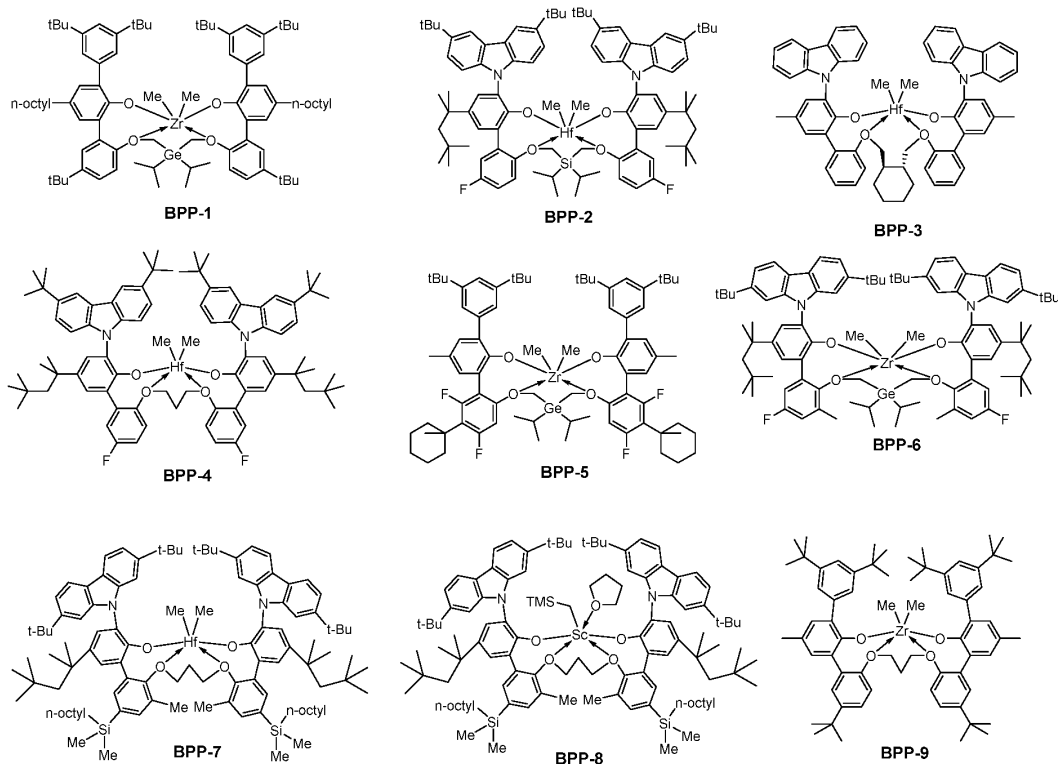
[0050] In formula (V), M^2 is titanium, zirconium, or hafnium. Each X^2 is independently selected from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_{3-j}(OR^C)_j$, $-Si(R^C)_{3-j}(OR^C)_j$, $-OSi(R^C)_{3-j}(OR^C)_j$, $-CH_2Ge(R^C)_{3-j}(OR^C)_j$, $-Ge(R^C)_{3-j}(OR^C)_j$, $-P(R^C)_{2-k}(OR^C)_k$, $-P(O)(R^C)_{2-k}(OR^C)_k$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^C Si(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$, $-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$, $-NHC(O)R^C$, $-C(O)N(R^C)_2$, $-C(O)NHR^C$, $-C(O)NH_2$, a halogen, $B(R^Y)_4$, $Al(R^Y)_4$, or $Ga(R^Y)_4$, or a hydrogen, wherein each R^C is independently a (C_1-C_{30}) hydrocarbyl, or (C_1-C_{30}) heterohydrocarbyl, and each j is 0, 1, 2 or 3, and each k is 0, 1, or 2; each R^Y is $-H$, (C_1-C_{30}) hydrocarbyl, or halogen atom, wherein two X^2 ligands can be connected to form a ring.

[0051] In some embodiments, in formula (V), A is $-C(R^{22})C(R^{23})-$, $-CH(R^{22})CH(R^{23})-$ or $-CH(R^{22})CH(R^{23})CH(R^{24})-$ and R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{30}) aryl, (C_5-C_{30}) heteroaryl, as defined hereinabove. In various embodiments, in formula (V), A is $-CH(R^{22})CH(R^{23})CH(R^{24})-$, and R^{23} and R^{24} may be connected to form an aromatic or non-aromatic ring, or R^{24} and R^{25} may be connected to form an aromatic or non-aromatic ring. In one or more embodiments, A is $-C(R^{22})C(R^{23})-$, and R^{23} and R^{25} may be connected to form an aromatic or non-aromatic ring. In some embodiments, in formula (V), A is $-C(R^{22})C(R^{23})-$. In one or more embodiments, in formula (V), A is $-CH(R^{22})CH(R^{23})CH(R^{24})-$.

[0052] In various embodiments, in formula (V), R^{22} , R^{23} , and R^{24} are (C_1-C_{20}) alkyl or $-H$, and R^{21} and R^{25} are substituted (C_6-C_{18}) aryl. In some embodiments, in formula (V), one of R^{22} , R^{23} , and R^{24} is selected from halogen atom, $-OMe$ and $-NMe_2$. In one or more embodiments, R^{22} , R^{23} , and R^{24} are independently selected from the group consisting of: methyl, ethyl, 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, dimethylamino, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl. In various embodiments, in formula (V), R^{26} , R^{27} , R^{28} , R^{29} , and R^{30} are each independently (C_1-C_{12}) alkyl, halogen substituted (C_1-C_{12}) alkyl, halogen substituted (C_6-C_{18}) aryl, halogen substituted (C_3-C_{50}) cycloalkyl, or $-H$.

[0053] As stated hereinabove, the molecular weight of the polymer produced by GD catalysts is much more sensitive to hydrogen than is the molecular weight of the polymer produced by BPP catalysts. Consequently, the molecular weight split (difference in molecular weight of the polyethylene produced by the two catalysts) can be easily tailored by adjusting hydrogen levels without significantly changing other conditions. The small changes in the hydrogen level results in large differences in molecular weight of the polymer produced by the GD catalyst. Comparatively, the same increases in H_2 lead to smaller changes in the molecular weight of the polymer produced by the BPP catalyst.

[0054] In illustrative embodiments, the catalyst systems may include a metal–ligand complex according to formula (I) having the structure of any of the procatalyst BPP-1, BPP-2, BPP-3, BPP-4, BPP-5, BPP-6, BPP-7, BPP-8, and BPP-9:



[0055] Cocatalyst Component

[0056] The catalyst system comprising a metal–ligand complex of formula (I) and formula (V) 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 formulas (I) and (V) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Additionally, the metal–ligand complex of formula (I) and formula (V) may include 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 a benzyl or phenyl. Suitable activating co-catalysts for use herein include alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a

trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0057] In some embodiments, the catalyst system does not include additives. An additive is a chemical agent present during the polymerization reaction that does not deter olefin propagation. In one or more embodiments, the catalyst system further comprises an additive. In some embodiments, the additives function as a co-catalyst. In other embodiments, the additives function as a scavenger or scavenging agent. A co-catalyst is a reagent that reacts in cooperation with a catalyst to catalyze the reaction or improve the catalytic activity of the catalyst. Without intent to be bound by theory, that when M_1 of formula (I) is scandium or yttrium, a ligand, Y, disassociates without the presence of a co-catalyst. However, it is also believed that a co-catalyst may promote the disassociation of any Lewis base present and coordinated to the metal center of the metal–ligand complex.

[0058] A scavenging agent sequesters impurities in the reactor prior to addition of the procatalyst, and as such, does not constitute an activator.

[0059] Suitable additives may include, but are not limited to, alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). Combinations of one or more of the foregoing additives and techniques are also contemplated.

[0060] Lewis acid activating co-catalysts include Group 13 metal compounds containing (C_1-C_{20}) hydrocarbyl substituents as described herein. In some embodiments, Group 13 metal compounds are tri((C_1-C_{20}) hydrocarbyl)-substituted-aluminum or tri((C_1-C_{20}) hydrocarbyl)-boron compounds. In other embodiments, Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum, tri((C_1-C_{20}) hydrocarbyl)-boron compounds, tri((C_1-C_{10}) alkyl)aluminum, tri((C_6-C_{18}) aryl)boron compounds, and halogenated (including perhalogenated) derivatives thereof. In further embodiments, Group 13 metal compounds are tris(fluoro-substituted phenyl)boranes, tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tris((C_1-C_{20}) hydrocarbenium borate (e.g. trityl tetrafluoroborate) or a tri((C_1-C_{20}) hydrocarbyl)ammonium tetra((C_1-C_{20}) hydrocarbyl)borate (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borate). As used herein, the term “ammonium” means a nitrogen cation that is a $((C_1-C_{20})\text{hydrocarbyl})_4N^+$, a $((C_1-C_{20})\text{hydrocarbyl})_3N(H)^+$, a $((C_1-C_{20})\text{hydrocarbyl})_2N(H)_2^+$, $(C_1-C_{20})\text{hydrocarbyl}N(H)_3^+$, or

$N(H)_4^+$, wherein each (C_1-C_{20}) hydrocarbyl, when two or more are present, may be the same or different.

[0061] Combinations of neutral Lewis acid activating co-catalysts include mixtures comprising a combination of a tri $((C_1-C_4)$ alkyl)aluminum and a halogenated tri $((C_6-C_{18})$ aryl)boron compound, especially a tris(pentafluorophenyl)borane. Other embodiments are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane. Ratios of numbers of moles of (metal–ligand complex): (tris(pentafluoro-phenylborane): (alumoxane) [e.g., (Group 4 metal–ligand complex) : (tris(pentafluoro-phenylborane): (alumoxane))] are from 1:1:1 to 1:10:30, in other embodiments, from 1:1:1.5 to 1:5:10.

[0062] The catalyst system that includes the metal–ligand complex of formulas (I) and (V) may be activated to form an active catalyst composition by combination with one or more cocatalysts, for example, a cation forming cocatalyst, a strong Lewis acid, or combinations thereof. Suitable activating co-catalysts include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate, and combinations thereof.

[0063] In some embodiments, more than one of the previously mentioned activating co-catalysts may be used in combination with each other. A specific example of a co-catalyst combination is a mixture of a tri $((C_1-C_4)$ hydrocarbyl)aluminum, tri $((C_1-C_4)$ hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound. The ratio of total number of moles of one or more metal–ligand complexes of formulas (I) and (V) to total number of moles of one or more of the activating co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some other embodiments, at least 1: 1000; and 10:1 or less, and in some other embodiments, 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, the number of moles of the alumoxane that are employed is at least 25 times the number of moles of the metal–ligand complex of formulas (I) and (V). When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, in some other embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal–ligand complexes of formulas (I) and (V) from 0.5:

1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal-ligand complexes of formulas (I) and (V).

[0064] Polymerization Process

[0065] Embodiments of this disclosure include process of producing ethylene-based polymers, the process comprising reacting ethylene and optionally one or more olefin monomers in one or more reactors in the presence of a catalyst system and optionally in the presence of hydrogen. In some embodiments, the process occurs in the presence of hydrogen. In one or more embodiments, the amount of hydrogen may be greater than 0 mmol. In embodiments, the amount of hydrogen may range from greater than 0 mmol to less than or equal to 1,000 mmol. In embodiments, the amount of hydrogen may range from greater than 0 mmol to less than or equal to 500 mmol, from greater than 0 mmol to less than or equal to 100 mmol, or from greater than 0 mmol to less than or equal to 10 mmol. In some embodiments, the hydrogen amount in mol%, which is the molar feed rate of fresh hydrogen / molar feed rate of fresh ethylene * 100, is from greater than 0.0 mol% to 4 mol%.

[0066] Any conventional polymerization processes may be employed to produce the polyolefin composition according to the present disclosure. Such conventional polymerization processes include, but are not limited to, solution polymerization process, particle forming polymerization process, and combinations thereof using one or more conventional reactors e.g. loop reactors, isothermal reactors, fluidized bed reactors, stirred tank reactors, batch reactors in parallel, series, and/or any combinations thereof. In various embodiments, the polymerization process is a solution polymerization reaction.

[0067] In one embodiment, the polyolefin composition according to the present disclosure may, for example, be produced via solution-phase polymerization process using one or more loop reactors, isothermal reactors, and combinations thereof.

[0068] In general, the solution phase polymerization process occurs in one or more well-stirred reactors such as one or more loop reactors or one or more spherical isothermal reactors at a temperature in the range of from 120 °C to 300 °C; from 120 °C to 250 °C; from 150 to 300 °C; from 150 °C to 250 °C; or from 160 °C to 215 °C, and at pressures in the range of from 300 to 1500 psi; for example, from 400 to 750 psi. The residence time in solution phase polymerization process is typically in the range of from 2 to 30 minutes; for example, from 5 to 15 minutes. Ethylene, one or more solvents, one or more high temperature olefin polymerization catalyst

systems, one or more cocatalysts and/or scavengers, and optionally one or more comonomers are fed continuously to the one or more reactors. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR E from ExxonMobil Chemical Co., Houston, Texas. The resultant mixture of the ethylene-based polymer and solvent is then removed from the reactor and the ethylene-based polymer is isolated. Solvent is typically recovered via a solvent recovery unit, i.e. heat exchangers and vapor liquid separator drum, and is then recycled back into the polymerization system.

[0069] In one embodiment, the ethylene-based polymer may be produced via solution polymerization in a single reactor system, for example a single loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of one or more high temperature olefin polymerization catalyst systems, optionally one or more other catalysts, and optionally one or more cocatalysts. 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 one or more an olefin polymerization catalyst systems, optionally one or more other catalysts, and optionally one or more cocatalysts. 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 one or more high temperature olefin polymerization catalyst systems, as described herein, in both reactors.

[0070] Polyolefins

[0071] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene-based polymers. In some embodiments, there is only ethylene in the polymerization scheme, creating an ethylene 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.

[0072] The ethylene-based polymers may comprise at least 60 weight percent monomer units derived from ethylene; at least 70 weight percent monomer units derived from ethylene; at least 80 weight percent monomer units derived from ethylene; or from 50 to 100 weight percent monomer units derived from ethylene; or from 80 to 100 weight percent units derived from ethylene. 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.

[0073] In some embodiments of the ethylene-based polymer, the amount of additional α -olefin is less than 50%; other embodiments include at least 0.5 mole percent (mol%) to 25 mol%; and in further embodiments the amount of additional α -olefin includes at least 5 mol% to 10 mol%. In some embodiments, the additional α -olefin is 1-octene.

[0074] 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.

[0075] The ethylene-based polymer may have a density according to ASTM D792 (incorporated herein by reference in its entirety) from 0.850 g/cm³ to 0.960 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, for example.

[0076] **Gel Permeation Chromatography (GPC)**

[0077] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the column and detector compartment were set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0078] 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 pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C 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)).:

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

where M is the molecular weight, A has a value of 0.41 and B is equal to 1.0.

[0079] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[0080] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

[0081] 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.

[0082] 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.

$$Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (\text{Equation 2})$$

$$Mw_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (\text{Equation 3})$$

$$Mz_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (\text{Equation 4})$$

[0083] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 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.

$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (\text{Equation 5})$$

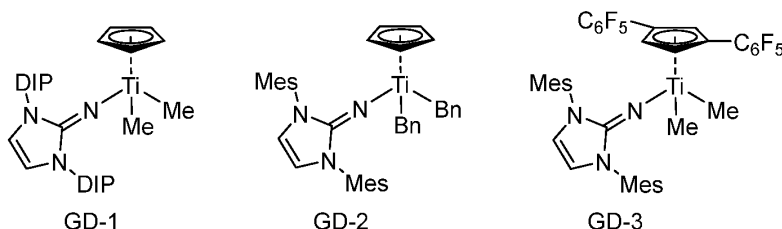
[0084] Chain transfer constant calculations

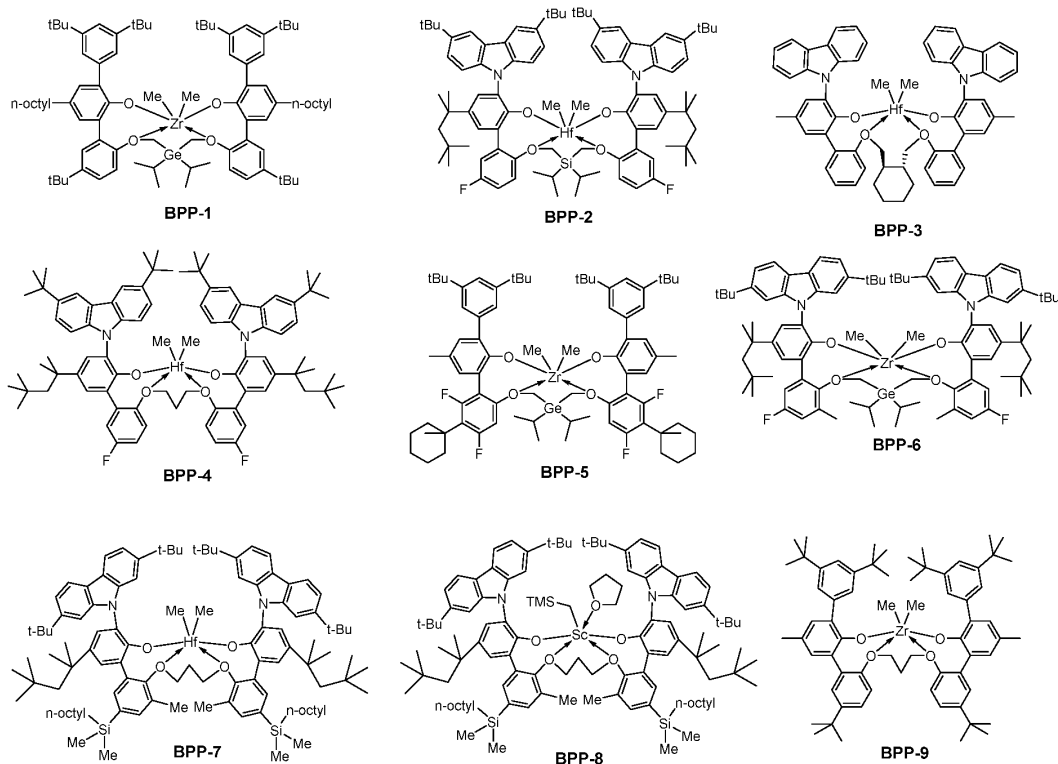
[0085] Chain transfer constant were calculated using the version of the Mayo equation shown in Equation 6 where Mn_0 is the Mn without any hydrogen added to the reactor, the H_2 and ethylene concentrations are liquid phase concentrations, and c_{CTH} is the ratio of the hydrogenolysis rate constant over the propagation rate constant. The reactor volume was 3.414 L, the liquid phase ethylene concentration was estimated to be 0.539 M, and the estimated hydrogen concentrations are: 1.17 mM, 2.31 mM, 4.53 mM, 8.74 mM, and 16.3 mM for 10, 20, 40, 80, and 160 mmol H_2 , respectively. The Mn values were calculated using Equation 6 for each loading of hydrogen. The Solver feature of MS Excel was used to vary the value of c_{CTH} to minimize the sum of the squared deviations of the calculated Mn values versus the experimental Mn values for all the hydrogen loadings simultaneously.

$$\frac{1}{Mn} = \frac{1}{Mn_0} + c_{CTH} \frac{[H_2]}{28 \times [ethylene]} \quad (\text{Equation 6})$$

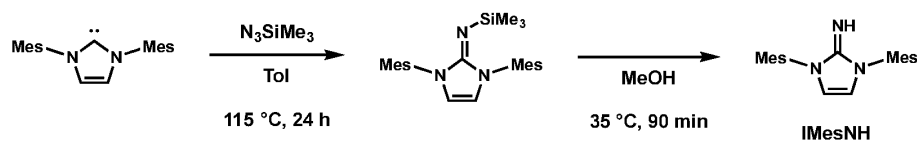
EXAMPLES

[0086] One or more features of the present disclosure are illustrated in view of the examples as follows:



**[0087] Synthetic Protocols**

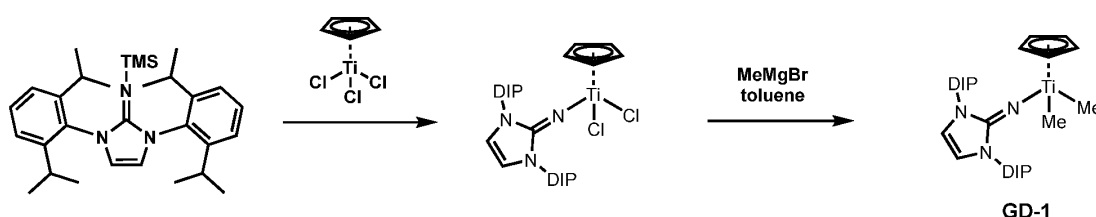
[0088] All commercial chemicals were used without further purification. All syntheses were performed in a continuous nitrogen purge glovebox unless otherwise stated. (Cyclopentadienyl)titanium(IV) tribenzyl (CpTiBn_3) was prepared by the reaction of 3 equivalents of benzylmagnesium chloride with one equivalent of (cyclopentadienyl)titanium(IV) trichloride. (Pentamethylcyclopentadienyl)titanium(IV) tribenzyl (Cp^*TiBn_3) was prepared by the reaction of 3 equivalents of benzylmagnesium chloride with one equivalent of (pentamethylcyclopentadienyl)titanium(IV) trichloride.

[0089] Synthesis of 1,3-dimesitylimidazol-2-imine (IMesNH)

[0090] In a nitrogen purge glovebox, 1,3-di-mesityl-imidazol-2-ylidene (1.13 g, 3.71 mmol, 1 equiv) was dissolved in toluene at ambient temperature. After stirring for 5 min, trimethylsilylazide (0.69 mL, 5.20 mmol, 1.4 equiv) was added dropwise. The reaction mixture was heated to 115 °C and stirred for 24 h. The reaction was cooled to ambient temperature, filtered

through a PTFE filter syringe, and concentrated. The residue was triturated with hexanes (2 x 2 mL) and dried in vacuo. The resulting solid was combined with methanol (2.25 mL, 15 equiv) and stirred at 35 °C for 90 min. The volatiles were removed in vacuo and the resulting crude material was then triturated with hexanes (2 x 4 mL), washed with warm (35 °C) hexanes (75 mL), and dried under vacuum. Yield: 0.560 g, 47%. ¹H NMR (400 MHz, C₆D₆) δ 6.77 (s, 4H), 5.72 (s, 2H), 4.28 (s, 1H), 2.24 (s, 12H), 2.12 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 151.7, 137.7, 137.2, 134.3, 129.2, 112.0, 20.8, 17.9.

[0091] Synthesis of GD-1

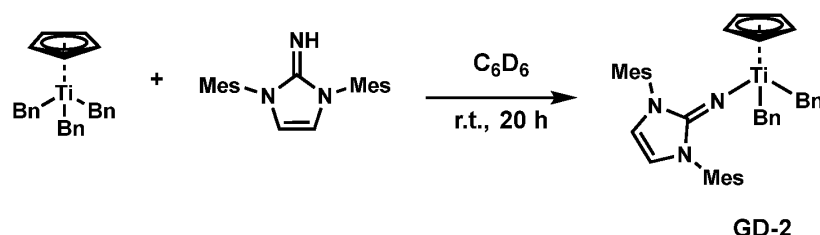


[0092] Step 1: In a N₂ atmosphere glove box, to a 40-mL vial equipped with a stir bar, was added 1,3-bis(2,6-diisopropylphenyl)-N-trimethylsilyl-imidazol-2-imine (0.300 g, 0.631 mmol) and trichloro(cyclopenta-2,4-dien-1-yl)titanium (0.138 g, 0.631 mmol) in 5 mL of dry degassed toluene. The vial was fitted with a small reflux condenser then the orange-yellow colored reaction mixture was heated at 80°C for 3 hours. Everything solubilized at elevated temperature. After this time the reaction was cooled to room temperature then 20 mL of pentane was added. The vial was placed in a freezer (−35 °C) for 6 days. The yellow precipitate was isolated by filtration and washed with cold pentane (3 x 5 mL). The resulting yellow solid was dried under vacuum to provide [[1,3-bis(2,6-diisopropylphenyl)2-midazole-2-ylidene]amino]-dichloro-cyclopenta-2,4-dien-1-yl-titanium (0.321 g, 0.547 mmol, yield: 87 %): ¹H NMR (400 MHz, benzene-d₆) δ 7.24 (dd, J = 8.5, 6.9 Hz, 2H), 7.13 (d, J = 1.0 Hz, 2H), 5.93 (s, 4H), 5.76 (s, 2H), 2.94 (hept, J = 6.8 Hz, 4H), 1.49 (d, J = 6.8 Hz, 12H), 1.07 (d, J = 6.9 Hz, 12H).

[0093] Step 2: In a N₂ atmosphere glove box to a 40-mL vial equipped with a stir bar was added [[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]amino]-dichloro-cyclopenta-2,4-dien-1-yl-titanium (0.300 g, 0.512 mmol) and 10 mL of dry degassed toluene. The vial was placed in a freezer (−35 °C) for 15 minutes, after which time bromo(methyl)magnesium (3.00 mol/L, 0.358 mL, 1.07 mmol) was added slowly to the red suspension. The mixture tended towards yellow/brown with a small amount of precipitate. The reaction mixture was stirred at room temperature for 2 hours then after this time the reaction was concentrated to dryness. The material

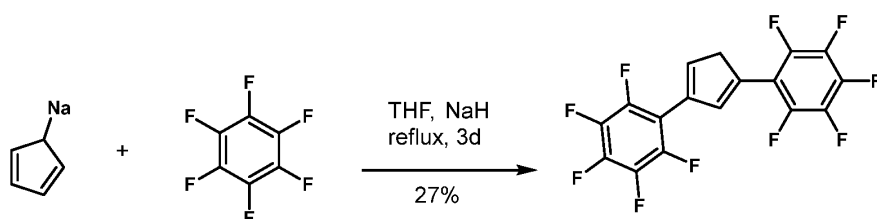
was taken up in toluene/pentane (15 mL, 4:1) then passed through a CELITE plug. The plug was further extracted with toluene/pentane (10 mL, 4:1). The combined yellow organic layers were concentrated to dryness to provide GD-1 (0.240 g, 0.440 mmol, yield: 86%) as a yellow powder; ^1H NMR (400 MHz, benzene- d_6) δ 7.22 (dd, J = 8.6, 6.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 4H), 5.89 (s, 2H), 5.73 (s, 5H), 3.24 – 3.09 (m, J = 6.6 Hz, 4H), 1.39 (d, J = 6.8 Hz, 12H), 1.15 (d, J = 6.9 Hz, 12H), 0.21 (s, 6H).

[0094] Synthesis of GD-2



[0095] Inside a nitrogen purge glovebox, CpTiBn_3 (50 mg, 0.13 mmol, 1 equiv) was combined with C_6D_6 (0.4 mL) and a stir bar. The mixture was allowed to stir at ambient temperature for 5 min until all the material had dissolved, affording a deep red solution. Separately, IMesNH (41 mg, 0.13 mmol, 1 equiv) was dissolved in C_6D_6 (0.3 mL). The nearly colorless solution of ligand was then added dropwise to the Ti-containing solution at ambient temperature while stirring. An additional ~0.3 mL of C_6D_6 was used to extract and transfer any residual ligand from its original vial to the reaction mixture. The resulting dark red-brown and homogeneous mixture was allowed to continue stirring at ambient temperature for 20 h. After this time, the reaction mixture was concentrated to an orange-red residue that was then triturated with hexanes (2 x 2 mL) and dried under vacuum. The material was taken up in toluene (2 mL), filtered, and concentrated to half the volume. Hexanes was added to the concentrated toluene solution causing mild turbidity. The contents of the vial were mixed thoroughly and then stored at $-25\text{ }^\circ\text{C}$ for 24 h. The precipitated material was collected and dried in vacuo. Yield: 74 mg, 93 %. ^1H NMR (400 MHz, C_6D_6) δ 7.19 – 7.12 (m, overlapping with NMR solvent, 4H) 6.86 (tt, J = 7.2, 1.3 Hz, 2H), 6.77 (s, 4H), 6.72 (d, J = 7.3 Hz, 4H), 5.59 (s, 2H), 5.48 (s, 5H), 2.45 (d, J = 9.1 Hz, 2H), 2.21 (s, 12H), 2.18 (d, J = 9.2 Hz, 2H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 153.1, 142.0, 139.4, 136.8, 133.5, 129.5, 126.3, 120.3, 113.4, 113.1, 70.8, 21.0, 18.1.

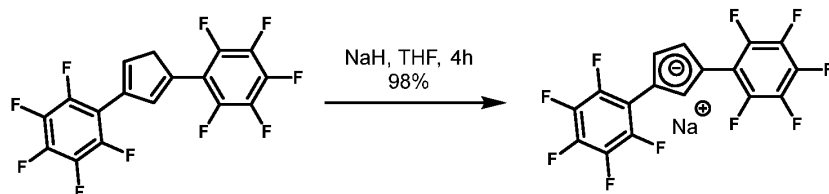
[0096] Synthesis of 6,6'-(cyclopenta-1,3-diene-1,3-diyl)bis(1,2,3,4,5-pentafluorobenzene)



[0097] A 250 mL round bottom flask was charged with Sodium Cyclopentadienylide (2.4 M in THF, 9.6 mL, 2.0 g, 0.023 mmol, 1 equiv), NaH (1.1 g, 0.046 mol, 2 equiv), C₆F₆ (42 g, 0.23 mol, 10 equiv), THF (100 mL), and a magnetic stir bar and the reaction mixture was refluxed under nitrogen for 3 d. The solvent was then removed under reduced pressure, and the residue was washed with pentane (3 × 50 mL). Pentane (100 mL) and water (20 mL) were added, the layers were separated, and the organic layer was dried over Na₂SO₄, filtered through neutral alumina, and evaporated to afford white solid. The white solid was dissolved in 50 mL hot ethanol and recrystallized to obtain needle shaped white crystals (2.5g, 27%).

[0098] ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.28 (m, 2H), 4.05 (p, *J* = 1.7 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -139.78 – -140.00 (m, 4H), -156.42 (t, *J* = 20.8 Hz, 2H), -162.55 (td, *J* = 21.1, 6.9 Hz, 4H).

[0099] Synthesis of (2,4-bis(perfluorophenyl)cyclopenta-2,4-dien-1-yl)sodium



[00100] In a N₂-filled glovebox, a 20 mL vial was charged with 6,6'-(cyclopenta-1,3-diene-1,3-diyl)bis(1,2,3,4,5-pentafluorobenzene) (500 mg, 1.25 mmol, 1 equiv), NaH (90 mg, 3.0 mmol, 3 equiv), 10 mL of dry THF, and a magnetic stir bar. Addition of NaH caused change in color of the reaction mixture from colorless to yellow. The reaction mixture was stirred at ambient temperature for 4h. Solvent was evaporated under reduced pressure to obtain faint yellow solid material. To the solid material, 10 mL of hexanes were added and filtered the solid to obtain solid residue which was then dried under vacuum to obtain white powder (125 mg, 98%).

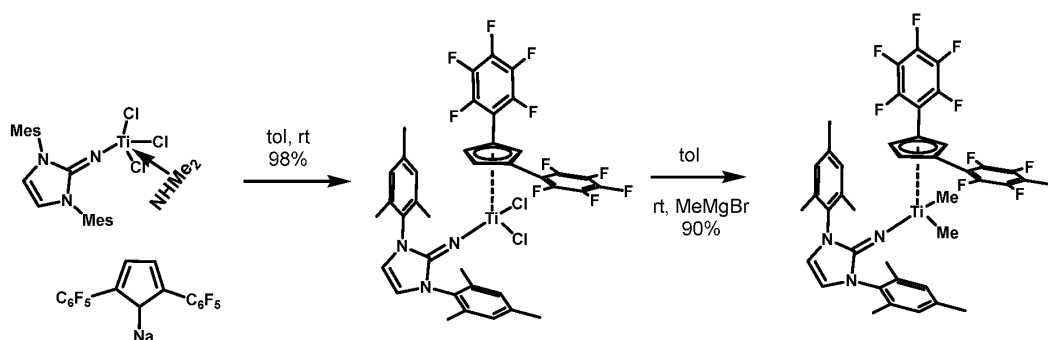
[00101] ¹H NMR (400 MHz, Benzene-*d*₆) δ 7.45 (p, *J* = 2.6 Hz, 1H), 6.95 (qd, *J* = 2.7, 1.7 Hz, 2H). ¹⁹F NMR (376 MHz, C₆D₆) δ -144.91 – -145.54 (m), -165.81 – -166.41 (m), -168.34 (t, *J* = 21.7 Hz).

[00102] Synthesis of IMesN(Me₂NH)TiCl₃



[00103] In a nitrogen filled glovebox, $(\text{Me}_2\text{N})\text{TiCl}_3$ (54 mg, 0.27 mmol, 1 equiv) was added to a 7 mL glass vial with Et_2O (8 mL) and a magnetic stir bar at ambient temperature. The mixture was allowed to stir at ambient temperature for 15 min. In a separate vial, (IMesNH) ligand (87 mg, 0.27 mmol, 1 equiv) was combined with Et_2O (6 mL). The faint yellow solution of ligand was then added dropwise at ambient temperature to the stirring solution of Ti precursor, causing a color change to bright red-orange along with an increase in turbidity. The heterogeneous red-orange suspension was then allowed to continue stirring at ambient temperature for 20 h. The bright orange solid was collected on a disposable frit, washed with Et_2O (2 x 4 mL) and pentane (2 x 3 mL). The orange solid further dried under vacuum and then stored at -25°C . Yield: 0.100 g, 70 %. ^1H NMR (500 MHz, C_6D_6) δ 6.82 (s, 4H), 5.37 (s, 2H), 2.75 (br s, 1H), 2.20 (s, 12H), 2.09 (s, 6H), 1.96 (s, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 140.3, 136.3, 131.5, 129.7, 128.4, 114.5, 21.1, 18.0.

[00104] Synthesis of GD-3



[00105] In a N_2 -filled glovebox, a 20 mL vial was charged with $\text{IMesN}(\text{Me}_2\text{NH})\text{TiCl}_3$ adduct (88 mg, 0.17 mmol, 1 equiv.), and 6 mL toluene was added. The sodium salt of the ligand (71.4 mg, 0.17 mmol, 1 equiv.) was dissolved in 7 mL toluene in another 20 mL vial. The Ti-precursor solution was added dropwise slowly to the sodium salts of the bis- $\text{C}_6\text{F}_5\text{Cp}$ ligand at room temperature. The color of the reaction mixture changed from white to reddish orange. The reaction was stirred for 2 hours at ambient temperature. The solvent was removed under vacuum. The solid insoluble yellow material was washed with 2:1 toluene:hexane (10 mL) thrice. The

residue was filtered through a fritted funnel to obtain orange powder which was dried under vacuum to afford the Ti-Cl₂ complex as an orange powder (140 mg, 98%).

[00106] ¹H NMR (500 MHz, C₆D₆) δ 7.42 (s, 1H), 6.83 (s, 4H), 6.17 (s, 2H), 5.38 (s, 2H), 2.15 (d, J = 9.7 Hz, 18H). ¹⁹F NMR (471 MHz, C₆D₆) δ -139.36 (d, J = 23.8 Hz), -156.67 (t, J = 21.7 Hz), -163.60 (t, J = 24.4 Hz).

[00107] In a N₂-filled glovebox, a 20 mL vial was charged with the Ti-Cl₂ complex (80 mg, 0.095 mmol, 1 equiv), 5 mL of toluene, and a stir bar. To the solution, MeMgBr in hexanes (0.076 mL of 3 (M) MeMgBr in hexanes, 0.23 mmol, 2.4 equiv) was added and the reaction mixture was stirred for 30 min at ambient temperature. The color of the reaction changes from orange to dark yellow upon addition of MeMgBr. The solution was filtered through a fritted funnel and a yellowish orange filtrate was obtained. The filtrate was evaporated under vacuum to obtain a light-yellow solid. To the light-yellow solid, 2 mL of toluene was added to dissolve the solid followed by addition of 10 mL of hexanes. The slurry was filtered through a fritted funnel to obtain a light-yellow filtrate. The solvent was removed to afford GD-3 as a light-yellow solid (68 mg, 90%).

[00108] ¹H NMR (400 MHz, C₆D₆) δ 7.59 – 7.52 (m, 1H), 6.80 (s, 4H), 5.89 (s, 2H), 5.55 (s, 2H), 2.15 (d, J = 9.6 Hz, 18H), 0.06 (s, 6H). ¹⁹F NMR (376 MHz, C₆D₆) δ -62.32 – -243.56 (m).

[00109] Polymerization Reactions

[00110] The results of the polymerization reactions of exemplary guanidine procatalysts in combination with exemplary bis(biphenylphenoxy) procatalysts are tabulated and discussed.

[00111] Raw materials (ethylene, 1-octene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent trademarked ISOPAR E commercially available from ExxonMobil Corporation) are purified with molecular sieves before introduction into the reaction environment. A one gallon (3.79 L) stirred autoclave reactor was charged with ISOPAR E, and 1-octene. The reactor was then heated to the desired temperature and charged with ethylene to reach the desired pressure. Hydrogen was also added at this point if desired. The catalyst composition was prepared in a drybox under inert atmosphere by mixing the desired pro-catalyst and optionally one or more additives as desired, with additional solvent to give a total volume of about 15-20 mL. The activated catalyst mixture was then quick-injected into the reactor. The reactor pressure and temperature were kept constant by feeding ethylene during the polymerization and cooling the reactor as needed. After 10 minutes, the ethylene feed was shut off and the solution transferred into a nitrogen-purged resin kettle. The polymer was thoroughly dried in a vacuum oven, and the reactor was thoroughly rinsed with hot ISOPAR E between polymerization runs.

[00112] Polymerization conditions: 3.79L (1 Gal) batch reactor, 1250 g of Isopar-E; combined procatalyst (formulas (I) and (V)):activator = 1:1.2; activator: $[(\text{HNMe}(\text{C}_{18}\text{H}_{37})_2)[\text{B}(\text{C}_6\text{F}_5)_4]]$; an Al-containing co-catalyst was used in a given ratio of Al:total metal (combined formulas (I) and (V)), either butylated hydroxy toluene-triethylaluminum 2:1 adduct (BHT-TEA) or MMAO that is modified with n-octyl substituents such that the methyl:n-octyl ratio is approximately 6:1; reaction time 10 min. 160 °C: 60 g 1-octene; ethylene, pressure to reach 320 psi. 190 °C: 65 g 1-octene; ethylene, pressure to reach 410 psi. The change of the weight average molecular weight with the incorporation of hydrogen gas at 160 °C was recorded in Table 1 for various exemplary GD procatalysts and various exemplary BPP procatalysts.

Table 1: Change of Weight Average Molecular Weight with the incorporation of Hydrogen Gas at 160 °C

Catalyst	M _w at 0 mmol of H ₂ (g/mol)	M _w at 10 mmol H ₂ (g/mol)	M _w at 20 mmol of H ₂ (g/mol)	M _w at 40 mmol of H ₂ (g/mol)	M _w at 80 mmol of H ₂ (g/mol)	M _w at 160 mmol of H ₂ (g/mol)
GD-1	239,509	32,940	17,102	10,503	6,015	--
GD-2	165,653	48,005	28,782	16,074	9,000	4,936
GD-3	168,211	26,532	15,811	7,815	4,911	--
BPP-1	1,695,000	473,600	444,900	264,400	--	--
BPP-2	892,900	664,800	509,600	485,900	--	--
BPP-3	928,400	694,600	565,300	361,000	263,700	142,800
BPP-4	557,100	--	--	407,100	--	--
BPP-5	1,291,000	--	--	219,800	--	--
BPP-7	693,600	610,600	547,100	451,500	354,100	146,000
BPP-8	232,000	183,100	162,200	104,700	68,600	40,800
BPP-9	459,600	361,700	277,100	203,600	129,500	76,400

[00113] The change of the weight average molecular weight with the incorporation of hydrogen gas at 190 °C was recorded in Table 2 for various exemplary GD procatalysts and various exemplary BPP procatalysts.

Table 2: Change of Weight Average Molecular Weight with the incorporation of Hydrogen Gas at 190 °C

Catalyst	M _w at 0 mmol of H ₂ (g/mol)	M _w at 10 mmol H ₂ (g/mol)	M _w at 20 mmol of H ₂ (g/mol)	M _w at 40 mmol of H ₂ (g/mol)	M _w at 80 mmol of H ₂ (g/mol)	M _w at 160 mmol of H ₂ (g/mol)
GD-1	--	47,180	19,677	8,624	5,275	--
GD-2	134,782	41,821	24,146	13,587	7,256	3,992
GD-3	42,814	25,821	17,071	9,443	--	--

BPP-1	570,000	439,200	303,100	179,700	--	--
BPP-2	559,500	538,200	482,500	408,500	--	--
BPP-3	356,200	263,800	178,700	163,000	100,100	47,700
BPP-4	276,300	--	--	247,900	--	--
BPP-5	612,300	--	--	142,000	--	--
BPP-6	--	496,000	416,700	254,300	189,100	94,600
BPP-7	414,500	380,100	344,100	290,600	211,500	154,300
BPP-9	289,000	218,400	186,600	140,000	94,400	63,000

[00114] The constants for chain transfer to hydrogen for various exemplary GD procatalysts and various exemplary BPP procatalysts are recorded in Table 3.

Table 3: Constants for Chain Transfer to Hydrogen (cH₂) for Selected Catalysts at 160 °C

Catalyst	cH ₂
GD-1	0.766
GD-2	0.395
GD-3	0.961
BPP-2	0.011
BPP-3	0.0078
BPP-7	0.0357
BPP-8	0.0158
BPP-9	0.0124

[00115] The number average molecular weight (M_n), weight average molecular weight (M_w), and z-average molecular weight (M_z) of the polymer composition produced by GD-1 and BPP-1 at four different concentrations of hydrogen at 160 °C are recorded in Table 4.

Table 4: Polymer Composition Produced by GD-1 and BPP-1 at four different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading (mmol)	M _n (g/mol)	M _w (g/mol)	M _z (g/mol)	M _w /M _n	M _z /M _n
C1	GD-1	5	23,602	52,340	121,791	2.22	5.16
C2	BPP-1	5	270,361	627,996	1,161,644	2.32	4.30
I1	GD-1/BPP-1	5	43,111	340,801	1,002,481	7.91	23.3
I2	GD-1/BPP-1	20	18,690	199,549	512,856	10.7	27.4
I3	GD-1/BPP-1	40	21,055	163,265	326,186	7.75	15.5

BHT-TEA used at 50 ratio (Al:total metal of formulas (I) and (V))

[00116] The M_n, M_w, and M_z of the polymer composition produced by GD-1 and BPP-2 at four different concentrations of hydrogen at 190 °C are recorded in Table 5.

Table 5: Polymer Composition Produced by GD-1 and BPP-2 at four different Hydrogen Loadings at 190 °C

	Catalyst(s)	Hydrogen Loading	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mn
C3	GD-1	5	19,554	45,050	123,419	2.30	6.31
C4	BPP-2	5	203,472	450,614	821,127	2.21	4.04
I4	GD-1/BPP-2	5	33,229	183,734	737,568	5.53	22.2
I5	GD-1/BPP-2	20	13,088	180,664	572,490	13.8	43.7
I6	GD-1/BPP-2	40	10,352	200,398	519,713	19.4	50.2

BHT-TEA used at 50 ratio (Al:total metal of formulas (I) and (V))

[00117] The Mn, Mw, and Mz of the polymer composition produced by GD-2 and BPP-1 at four different concentrations of hydrogen at 160 °C are recorded in Table 6.

Table 6: Polymer Composition Produced by GD-2 and BPP-1 at four different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mn
I7	GD-2/BPP-1	5	41,895	191,608	714,041	4.57	17.0
I8	GD-2/BPP-1	20	21,634	147,105	566,993	6.80	26.2
I9	GD-2/BPP-1	40	12,868	99,978	357,759	7.77	27.8

MMAO at 20 ratio (Al:total metal of formulas (I) and (V))

[00118] The Mn, Mw, and Mz of the polymer composition produced by GD-3 and BPP-1 at four different concentrations of hydrogen at 160 °C are recorded in Table 7.

Table 7: Polymer Composition Produced by GD-3 and BPP-1 at four different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mn
C5	GD-3	5	10,332	26,795	80,894	2.59	7.83
C6	BPP-1	5	270,361	627,996	1,161,644	2.32	4.30
I10	GD-3/BPP-1	5	13,864	240,554	888,126	17.4	64.1
I11	GD-3/BPP-1	20	9,913	181,290	527,768	18.3	53.2
I12	GD-3/BPP-1	40	5,620	111,114	303,190	19.8	54.0

MMAO at 20 ratio (Al:total metal of formulas (I) and (V))

[00119] Referring to Table 1, where the catalysts were evaluated at 160 °C, when 10 mmol of hydrogen gas was first added to the catalysts of GD-1, GD-2, and GD-3, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 70 wt.% and 90 wt.% compared to the resulting polymers of the GD catalysts that were not exposed to hydrogen. However, the M_w of the resulting polymers of the BPP catalysts only dropped from about 10 wt.%

to 25 wt.% compared to the resulting polymers of the BPP catalysts that were not exposed to hydrogen.

[00120] Similarly, in Table 1, when the amount of hydrogen was increased from 10 mmol to 20 mmol, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 40 wt.% and 50 wt.%, whereas the resulting polymers of the BPP catalysts only dropped between about 10 wt.% and 25 wt.%. This suggests that the BPP catalysts are not as sensitive to the increased hydrogen as the GD catalysts.

[00121] Furthermore, in Table 1, when the amount of hydrogen was increased from 20 mmol to 40 mmol, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 35 wt.% and 50 wt.%, whereas the resulting polymers of the BPP catalysts only dropped between about 5 wt.% and 40 wt.%. Again, this suggests that the BPP catalysts are not as sensitive to the increased hydrogen as the GD catalysts.

[00122] Referring now to Table 2, where the catalysts were evaluated at 190 °C, when 10 mmol of hydrogen gas was first added to the catalysts of GD-1, GD-2, and GD-3, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 40 wt.% and 85 wt.% compared to the resulting polymers of the GD catalysts that were not exposed to hydrogen. However, the M_w of the resulting polymers of the BPP catalysts only dropped from about 5 wt.% to 25 wt.% compared to the resulting polymers of the BPP catalysts that were not exposed to hydrogen.

[00123] Similarly, in Table 2, when the amount of hydrogen was increased from 10 mmol to 20 mmol, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 35 wt.% and 45 wt.%, whereas the resulting polymers of the BPP catalysts only dropped between about 10 wt.% and 30 wt.%. This suggests that the BPP catalysts are not as sensitive to the increased hydrogen as the GD catalysts.

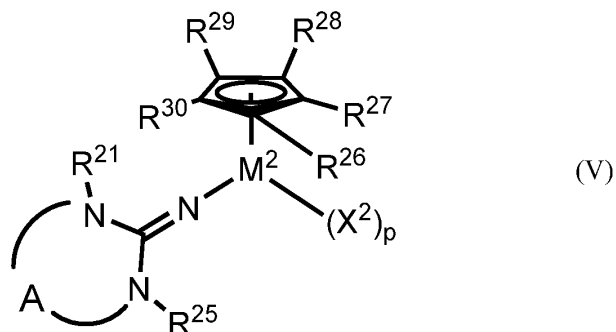
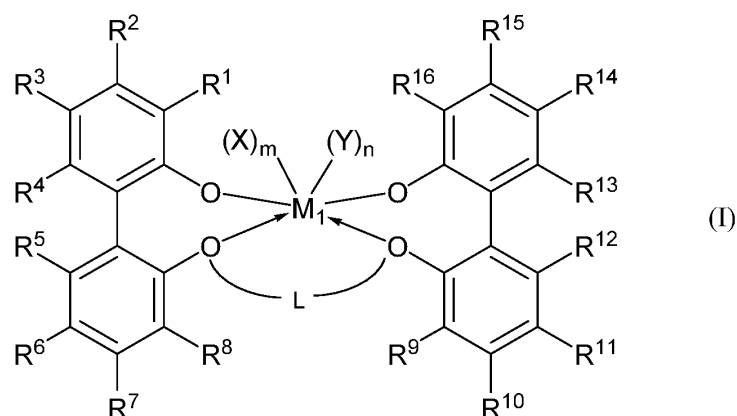
[00124] Furthermore, in Table 1, when the amount of hydrogen was increased from 20 mmol to 40 mmol, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 40 wt.% and 50 wt.%, whereas the resulting polymers of the BPP catalysts only dropped between about 5 wt.% and 40 wt.%. Again, this suggests that the BPP catalysts are not as sensitive to the increased hydrogen as the GD catalysts.

[00125] Additionally, as shown in FIGs. 2-5, the GD catalysts are more sensitive to the introduction of hydrogen than the BPP catalysts. In FIGs. 2-5, each catalyst system at a given hydrogen concentration has two peaks. The peak with the lowest LogM represents the product

created by the GD catalyst, and the peak with the highest LogM represents the product created by the BPP catalyst. As shown in each of FIGs. 2-5, when the hydrogen concentration is increased from 5 mmol to 20 mmol, the LogM of the peak created by the BPP catalyst decreases slightly, whereas the LogM of the peak created by the GD catalyst decreases more significantly. Similarly, when the hydrogen concentration is further increased from 20 mmol to 40 mmol, the LogM of the peak created by the BPP catalyst again decreases slightly, whereas the LogM of the peak created by the GD catalyst decreases more significantly. Thus, the slight decrease in LogM of the peak created by the BPP catalyst compared to the more significant decrease in LogM of the peak created by the GD catalyst demonstrates that GD catalysts are more sensitive than BPP catalysts to changes in hydrogen concentration.

CLAIMS

1. A process of producing ethylene-based polymers, the process comprising reacting ethylene and optionally one or more olefin monomers in one or more reactors in the presence of a catalyst system and optionally in the presence of hydrogen; the catalyst system comprises two or more catalysts, at least one of which is derived from a bis(biphenylphenoxy) procatalyst according to formula (I) and at least one of which is derived from a guanidine procatalyst according to formula (V):



where, in formula (I):

M_1 is titanium, zirconium, hafnium, scandium or yttrium;

each X is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbyl,

(C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$,

$-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, $-CH_2Ge(R^C)_{3-Q}(OR^C)_Q$,

$-Ge(R^C)_{3-Q}(OR^C)_Q$, $-P(R^C)_{2-W}(OR^C)_W$, $-P(O)(R^C)_{2-W}(OR^C)_W$, $-N(R^C)_2$, $-NH(R^C)$,

$-N(Si(R^C)_3)_2$, $-NR^C Si(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$,

$-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$,

$-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$,

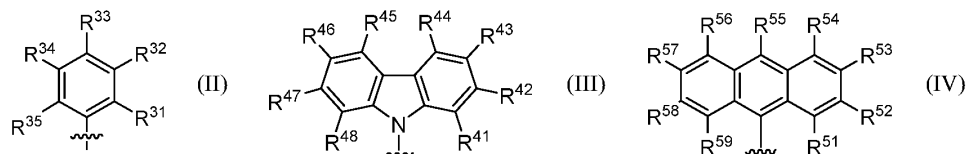
$-\text{NHC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{N}(\text{R}^{\text{C}})_2$, $-\text{C}(\text{O})\text{NHR}^{\text{C}}$, $-\text{C}(\text{O})\text{NH}_2$, a halogen, $\text{B}(\text{R}^{\text{Y}})_4$, $\text{Al}(\text{R}^{\text{Y}})_4$, or $\text{Ga}(\text{R}^{\text{Y}})_4$, or a hydrogen, wherein each R^{C} is independently a $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, or $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, and each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^{Y} is $-\text{H}$, $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, or halogen atom; each Y is independently a Lewis Base; optionally, X and Y can be linked to form a ring. m is 1 or 2;

n is 0, 1, or 2;

p is 0, 1, or 2;

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):



where 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;

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:

in formula (V), M^2 is titanium, zirconium, or hafnium;

each X^2 is independently selected from $(\text{C}_1-\text{C}_{50})$ hydrocarbyl,

$(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl, $-\text{CH}_2\text{Si}(\text{R}^{\text{C}})_3(\text{OR}^{\text{C}})_j$,

$-\text{Si}(\text{R}^{\text{C}})_{3-\text{J}}(\text{OR}^{\text{C}})_{\text{J}}$, $-\text{OSi}(\text{R}^{\text{C}})_{3-\text{J}}(\text{OR}^{\text{C}})_{\text{J}}$, $-\text{CH}_2\text{Ge}(\text{R}^{\text{C}})_{3-\text{J}}(\text{OR}^{\text{C}})_{\text{J}}$, $-\text{Ge}(\text{R}^{\text{C}})_{3-\text{J}}(\text{OR}^{\text{C}})_{\text{J}}$,
 $-\text{P}(\text{R}^{\text{C}})_{2-\text{K}}(\text{OR}^{\text{C}})_{\text{K}}$, $-\text{P}(\text{O})(\text{R}^{\text{C}})_{2-\text{K}}(\text{OR}^{\text{C}})_{\text{K}}$, $-\text{N}(\text{R}^{\text{C}})_2$, $-\text{NH}(\text{R}^{\text{C}})$, $-\text{N}(\text{Si}(\text{R}^{\text{C}})_3)_2$,
 $-\text{NR}^{\text{C}}\text{Si}(\text{R}^{\text{C}})_3$, $-\text{NHSi}(\text{R}^{\text{C}})_3$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $-\text{OCF}_3$, $-\text{S}(\text{O})\text{R}^{\text{C}}$,
 $-\text{S}(\text{O})_2\text{R}^{\text{C}}$, $-\text{OS}(\text{O})_2\text{R}^{\text{C}}$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $-\text{N}=\text{CH}(\text{R}^{\text{C}})$, $-\text{N}=\text{CH}_2$, $-\text{N}=\text{P}(\text{R}^{\text{C}})_3$,
 $-\text{OC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{OR}^{\text{C}}$, $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{R}^{\text{C}}$, $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{H}$, $-\text{NHC}(\text{O})\text{R}^{\text{C}}$,
 $-\text{C}(\text{O})\text{N}(\text{R}^{\text{C}})_2$, $-\text{C}(\text{O})\text{NHR}^{\text{C}}$, $-\text{C}(\text{O})\text{NH}_2$, a halogen, $\text{B}(\text{R}^{\text{Y}})_4$, $\text{Al}(\text{R}^{\text{Y}})_4$, or $\text{Ga}(\text{R}^{\text{Y}})_4$,
 or a hydrogen, wherein each R^{C} is independently a $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, or
 $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, and each J is 0, 1, 2 or 3, and each K is 0, 1, or 2;
 each R^{Y} is $-\text{H}$, $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, or halogen atom, wherein two X^2 ligands
 can be connected to form a ring;

A is $-\text{C}(\text{R}^{22})\text{C}(\text{R}^{23})-$, $\text{CH}(\text{R}^{22})\text{CH}(\text{R}^{23})-$, or $-\text{CH}(\text{R}^{22})\text{CH}(\text{R}^{23})\text{CH}(\text{R}^{24})-$, and optionally:

R^{21} and R^{22} may be connected to form an aromatic or non-aromatic ring;
 or R^{22} and R^{23} may be connected to form an aromatic or non-aromatic
 ring; or

when A is $-\text{CH}(\text{R}^{22})\text{CH}(\text{R}^{23})\text{CH}(\text{R}^{24})-$, R^{23} and R^{24} may be connected to
 form an aromatic or non-aromatic ring, or R^{24} and R^{25} may be connected
 to form an aromatic or non-aromatic ring; or

when A is $-\text{C}(\text{R}^{22})\text{C}(\text{R}^{23})-$ or $-\text{CH}(\text{R}^{22})\text{CH}(\text{R}^{23})-$, R^{23} and R^{25} may be
 connected to form an aromatic or non-aromatic ring;

R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} are independently $(\text{C}_1-\text{C}_{50})$ hydrocarbyl,

$(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl, $(\text{C}_6-\text{C}_{30})$ aryl, $(\text{C}_5-\text{C}_{30})$ heteroaryl; and

R^{26} , R^{27} , R^{28} , R^{29} , and R^{30} are each independently $(\text{C}_1-\text{C}_{12})$ alkyl, halogen substituted

$(\text{C}_1-\text{C}_{12})$ alkyl, halogen substituted $(\text{C}_6-\text{C}_{18})$ aryl, halogen substituted $(\text{C}_3-\text{C}_{50})$
 cycloalkyl, or $-\text{H}$.

2. The polymerization process according to claim 1, wherein the polymerization process occurs in the presence of hydrogen feed.
3. The polymerization process according to claim 1, wherein the polymerization process occurs in the absence of hydrogen feed.
4. The polymerization process according to claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (II) or a radical having formula (III)
5. The polymerization process according to any of the preceding claims, wherein R^8 and R^9 are independently (C_1-C_4) alkyl.

6. The polymerization process according to any of the preceding claims, wherein R^3 and R^{14} are (C_1-C_{20}) alkyl,
7. The polymerization process according to any one of the preceding claims, wherein L is chosen from $-CH_2(CH_2)_mCH_2-$, $-CH_2Si(R^C)(R^D)CH_2-$, $-CH_2Ge(R^C)(R^D)CH_2-$, $-CH_2(CH_3)CH_2CH^*(CH_3)$, 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.
8. The polymerization process according to any one of the preceding claims, wherein A is $-C(R^{22})C(R^{23})-$ or $-C(R^{22})C(R^{23})C(R^{24})-$.
9. The polymerization process according to any one of the preceding claims, wherein R^{22} , R^{23} , and R^{24} are (C_1-C_{20}) alkyl or $-H$, and R^{21} and R^{25} are substituted (C_6-C_{18}) aryl.
10. The polymerization process according to any one of the preceding claims, wherein R^{22} , R^{23} , and R^{24} are independently selected from the group consisting of: methyl, ethyl, 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, methoxy, dimethylamino, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.
11. The polymerization process according to any one of the preceding claims, wherein the polymerization process is a solution polymerization reaction.