

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. 63/401,901 filed August 29, 2022, the entire disclosure of which is hereby incorporated herein by reference.

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 bis-phenylphenoxy Group IV transition metal catalysts and PN catalyst 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.

[0004] Ethylene-based polymers and propylene-based are manufactured for a wide variety of articles. The polyethylene and polypropylene polymerization process can be varied in a number of respects to produce a wide variety of resultant polyethylene resins having different physical properties that render the various resins suitable for use in different applications. The ethylene monomers and, optionally, one or more co-monomers are present in liquid diluents (such as solvents), such as an alkane or isoalkane, for example isobutene. Hydrogen may also be added to the reactor. The catalyst systems for producing ethylene-based homopolymer or copolymer may typically comprise a chromium-based catalyst system, a Ziegler–Natta catalyst system, and/or a molecular (either metallocene or non-metallocene (molecular)) catalyst system. The reactants in the diluent and the catalyst system are circulated at an elevated polymerization temperature around the reactor, thereby producing ethylene-based homopolymer or copolymer. Either periodically or continuously, part of the reaction mixture, including the polyethylene product dissolved in the diluent, together with unreacted ethylene

and one or more optional co-monomers, is removed from the reactor. The reaction mixture, when removed from the reactor, may be processed to remove the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor, serially connected to the first reactor, where a second polyethylene fraction may be produced. 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 polymer with molecular weights that can be adjusted during the polymerization process.

SUMMARY

[0005] Ongoing needs exist to produce a multimodal polyethylene polymer. Specifically, synthesizing LLDPE resins using a flexible catalyst system that is compatible with high temperature solution processes.

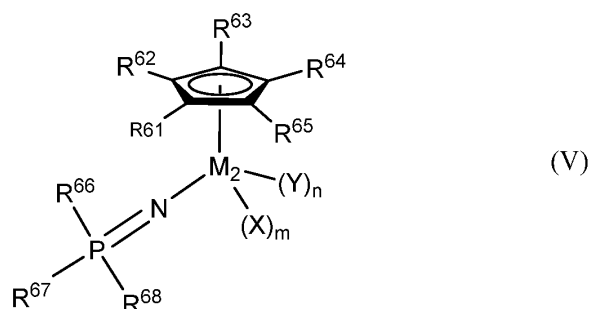
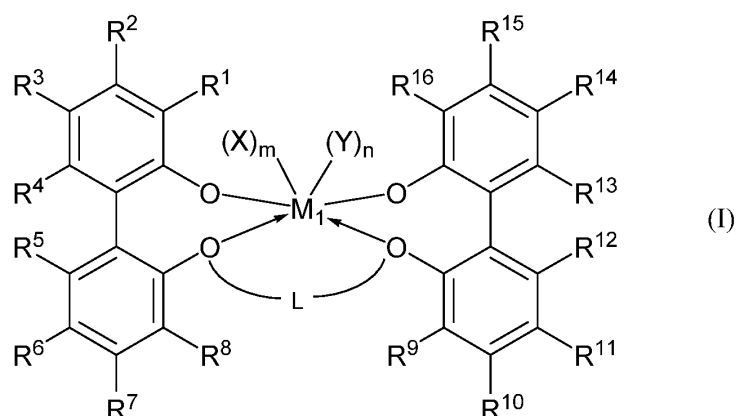
[0006] By combining catalysts derived from two different classes, such as bis-phenylphenoxy metal–ligand complexes (BPP catalysts) and phosphinimine complexes (PN catalysts), the advantages of the different properties of the catalysts allow the production of multimodal polyethylene resin.

[0007] The PN catalysts is much more sensitive to hydrogen than is by BPP catalysts, thus the molecular weight of the polymer produce by the PN catalyst may be altered based on the amount of hydrogen in the reactor system. 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 PN 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 BPP catalysts and the PN catalysts.

[0008] Embodiments of this disclosure include processes of polymerizing olefin monomers to produce polyolefin. The process includes reacting ethylene and optionally one or more olefin monomers in one reactor or multiple reactors in the presence of a catalyst system and optionally hydrogen gas. The catalyst includes two or more catalysts, at least one of which is derived from bis-phenylphenoxy procatalysts according to formula (I) and at least one of which

is derived from phosphininimine procatalyst according to formula (V). The amount of hydrogen gas may be adjusted to tailor the molecular weight of the polyolefin.

[0009] Formula (I) and formula (V) have structures according to:

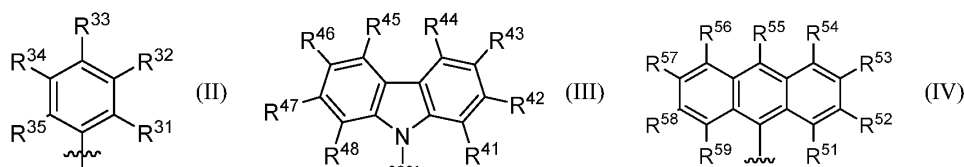


[0010] In formula (I), M_1 is titanium, zirconium, hafnium, scandium or yttrium.

[0011] In formula (I) and formula (V), 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 two X ligands can be connected to form a metallocycle ring.

[0012] In formulas (I) and (V), each Y is independently Lewis Base; optionally, X and Y can be linked to form a ring. Each Subscript m is independently 0, 1, or 2; and each subscript n is independently 0, 1 and 2.

[0013] 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):



[0014] 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.

[0015] 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.

[0016] In formula (I), L is (C_1-C_{40}) hydrocarbylene or (C_2-C_{40}) heterohydrocarbylene.

[0017] In formula (I), 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 $-H$.

[0018] In formula (V), M_2 is titanium, zirconium, or hafnium; R^{61} , R^{62} , R^{63} , R^{64} , and R^{65} are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl wherein any of the R^{62} , R^{63} , R^{64} , and R^{65} optionally are connected to form a ring structure; R^{66} , R^{67} , and R^{68} are independently (C_1-C_{20}) hydrocarbyl, (C_1-C_{20}) heterohydrocarbyl, (C_6-C_{30}) aryl, (C_5-C_{30}) heteroaryl wherein two of R^{66} , R^{67} , and R^{68} are optionally connected to form a ring.

BRIEF DESCRIPTION OF FIGURES

[0019] FIG. 1A shows two theoretical molecular weight distribution curves of two unimodal polymer compositions produced by a bis-phenylphenoxy catalyst and produced by a phosphinimine catalyst with no hydrogen gas in the reactor chamber.

[0020] FIG. 1B shows two theoretical molecular weight distribution curves of two unimodal polymer compositions produced by a bis-phenylphenoxy catalyst and produced by a phosphinimine catalyst with a small amount of hydrogen gas in the reactor chamber.

[0021] FIG. 1C shows two theoretical molecular weight distribution curves of two unimodal polymer compositions produced by a bis-phenylphenoxy catalyst and produced by a phosphinimine catalyst with a larger amount of hydrogen gas in the reactor chamber.

[0022] FIG. 2 is a graph of the molecular weight of polymers produced by three different phosphinimine catalysts as a function of the amount of hydrogen (mmol) in the reactor.

[0023] FIG. 3 is molecular weight distribution curve obtained from Gel Permeation Chromatography (GPC) of bimodal polymer compositions produced by a bis-phenylphenoxy catalyst (BPP-1) and a phosphinimine catalyst (PN-1) with varying amounts of hydrogen gas in the reactor chamber. The amounts of hydrogen are: 0 mmol of H₂, 5 mmol of H₂, 20 mmol of H₂, and 40 mmol of H₂.

[0024] FIG. 4 is GPC trace with comonomer distribution of the polyethylene produced by the dual catalyst (BPP-1 and PN-1).

[0025] FIG. 5 is GPC trace with comonomer distribution of dual catalyst-produced PE with PN-1 and BPP-2 at three hydrogen loadings at a temperature of 160°C.

[0026] FIG. 6 is GPC trace with comonomer distribution of dual catalyst-produced PE.

[0027] FIG. 7 is improved comonomer composition distribution (iCCD) data for dual catalyst produced PE with dual catalysts.

[0028] FIG. 8 is GPC trace with comonomer distribution of dual catalyst-produced PE with PN-1 and BPP-3 at three hydrogen loadings at a temperature of 160°C.

[0029] FIG. 9 is GPC trace with comonomer distribution of dual catalyst-produced PE with PN-1 and BPP-4 at three hydrogen loadings at a temperature of 160°C.

[0030] FIG. 10 is GPC trace with comonomer distribution of dual catalyst-produced PE with PN-1 and BPP-5 at three hydrogen loadings at a temperature of 160°C.

DETAILED DESCRIPTION

[0031] 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.

[0032] The term “independently selected” followed by multiple options is used herein to indicate that individual R groups appearing before the term, such as R^1 , R^2 , R^3 , R^4 , and R^5 , can be identical or different, without dependency on the identity of any other group also appearing before the term.

[0033] 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.

[0034] 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.

[0035] 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.

[0036] The term “(C₁-C₅₀)hydrocarbyl” means a hydrocarbon radical from 1 to 50 carbon atoms and the term “(C₁-C₅₀)hydrocarbylene” means a hydrocarbon diradical from 1 to 50 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (having three carbons or more, and including mono- and poly-cyclic, fused and non-fused polycyclic, and bicyclic) or acyclic, and substituted by one or more R^S or unsubstituted.

[0037] In this disclosure, a (C₁-C₅₀)hydrocarbyl may be an unsubstituted or substituted (C₁-C₅₀)alkyl, (C₃-C₅₀)cycloalkyl, (C₃-C₂₀)cycloalkyl-(C₁-C₂₀)alkylene, (C₆-C₄₀)aryl, or (C₆-C₂₀)aryl-(C₁-C₂₀)alkylene (such as benzyl (-CH₂-C₆H₅)).

[0038] The terms “(C₁-C₅₀)alkyl” and “(C₁-C₁₈)alkyl” mean a saturated straight or branched hydrocarbon radical of from 1 to 50 carbon atoms and a saturated straight or branched hydrocarbon radical of from 1 to 18 carbon atoms, respectively, that is unsubstituted or substituted by one or more R^S . 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, respectively. Each (C₁-C₅)alkyl may be methyl, trifluoromethyl, ethyl, 1-propyl, 1-methylethyl, or 1,1-dimethylethyl.

[0039] The term “(C₆-C₅₀)aryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic aromatic hydrocarbon radical of from 6 to 40 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms. A monocyclic aromatic

hydrocarbon radical includes one aromatic ring; a bicyclic aromatic hydrocarbon radical has two rings; and a tricyclic aromatic hydrocarbon radical has three rings. Examples of unsubstituted (C₆–C₅₀)aryl include: unsubstituted (C₆–C₂₀)aryl, unsubstituted (C₆–C₁₈)aryl; 2-(C₁–C₅)alkyl-phenyl; phenyl; fluorenyl; tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; and phenanthrene. Examples of substituted (C₆–C₄₀)aryl include: substituted (C₁–C₂₀)aryl; substituted (C₆–C₁₈)aryl; 2,4-bis([C₂₀]alkyl)-phenyl; polyfluorophenyl; pentafluorophenyl; and fluoren-9-one-1-yl.

[0040] The term “(C₃–C₅₀)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.

[0041] Examples of (C₁–C₅₀)hydrocarbylene include unsubstituted or substituted (C₆–C₅₀)arylene, (C₃–C₅₀)cycloalkylene, and (C₁–C₅₀)alkylene (e.g., (C₁–C₂₀)alkylene). The diradicals may be on the same carbon atom (e.g., –CH₂–) or on adjacent carbon atoms (i.e., 1,2-diradicals), or are spaced apart by one, two, or more than two intervening carbon atoms (e.g., 1,3-diradicals, 1,4-diradicals, etc.). Some diradicals include 1,2-, 1,3-, 1,4-, or an α,ω-diradical, and others a 1,2-diradical. The α,ω-diradical is a diradical that has maximum carbon backbone spacing between the radical carbons. Some examples of (C₂–C₂₀)alkylene α,ω-diradicals include ethan-1,2-diyl (i.e. –CH₂CH₂–), propan-1,3-diyl (i.e., –CH₂CH₂CH₂–), 2-methylpropan-1,3-diyl (i.e., –CH₂CH(CH₃)CH₂–). Some examples of (C₆–C₅₀)arylene α,ω-diradicals include phenyl-1,4-diyl, naphthalen-2,6-diyl, or naphthalen-3,7-diyl.

[0042] The term “(C₁–C₅₀)alkylene” means a saturated straight chain or branched chain diradical (i.e., the radicals are not on ring atoms) of from 1 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted (C₁–C₅₀)alkylene are unsubstituted (C₁–C₂₀)alkylene, including unsubstituted –CH₂CH₂–, –(CH₂)₃–, –(CH₂)₄–, –(CH₂)₅–, –(CH₂)₆–, –(CH₂)₇–, –(CH₂)₈–, –CH₂C*HCH₃, and –(CH₂)₄C*(H)(CH₃), in which “C*” denotes a carbon atom from which a hydrogen atom is removed to form a secondary or tertiary alkyl radical. Examples of substituted (C₁–C₅₀)alkylene are substituted (C₁–C₂₀)alkylene, –CF₂–, –C(O)–, and –(CH₂)₁₄C(CH₃)₂(CH₂)₅– (i.e., a 6,6-dimethyl substituted normal-1,20-eicosylene). Since as mentioned previously two R^S may be taken

together to form a (C₁–C₁₈)alkylene, examples of substituted (C₁–C₅₀)alkylene also include 1,2-bis(methylene)cyclopentane, 1,2-bis(methylene)cyclohexane, 2,3-bis(methylene)-7,7-dimethyl-bicyclo[2.2.1]heptane, and 2,3-bis(methylene)bicyclo[2.2.2]octane.

[0043] The term “(C₃–C₅₀)cycloalkylene” means a cyclic diradical (i.e., the radicals are on ring atoms) of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S.

[0044] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of groups containing one or more than one heteroatom include O, S, S(O), S(O)₂, Si(R^C)₂, P(R^P), N(R^N), –N=C(R^C)₂, –Ge(R^C)₂–, or –Si(R^C)–, where each R^C and each R^P is unsubstituted (C₁–C₁₈)hydrocarbyl or –H, and where each R^N is unsubstituted (C₁–C₁₈)hydrocarbyl. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms of a hydrocarbon are replaced with a heteroatom. The term “(C₁–C₅₀)heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 50 carbon atoms, and the term “(C₁–C₅₀)heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 50 carbon atoms. The heterohydrocarbon of the (C₁–C₅₀)heterohydrocarbyl or the (C₁–C₅₀)heterohydrocarbylene has one or more heteroatoms. The radical of the heterohydrocarbyl may be on a carbon atom or a heteroatom. The two radicals of the heterohydrocarbylene may be on a single carbon atom or on a single heteroatom. Additionally, one of the two radicals of the diradical may be on a carbon atom and the other radical may be on a different carbon atom; one of the two radicals may be on a carbon atom and the other on a heteroatom; or one of the two radicals may be on a heteroatom and the other radical on a different heteroatom. Each (C₁–C₅₀)heterohydrocarbyl and (C₁–C₅₀)heterohydrocarbylene may be unsubstituted or substituted (by one or more R^S), aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic), or acyclic.

[0045] The (C₁–C₅₀)heterohydrocarbyl may be unsubstituted or substituted. Non-limiting examples of the (C₁–C₅₀)heterohydrocarbyl include (C₁–C₅₀)heteroalkyl, (C₁–C₅₀)hydrocarbyl-O–, (C₁–C₅₀)hydrocarbyl-S–, (C₁–C₅₀)hydrocarbyl-S(O)–, (C₁–C₅₀)hydrocarbyl-S(O)₂–, (C₁–C₅₀)hydrocarbyl-Si(R^C)₂–, (C₁–C₅₀)hydrocarbyl-N(R^N)–, (C₁–C₅₀)hydrocarbyl-P(R^P)–, (C₂–C₅₀)heterocycloalkyl, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)alkylene, (C₃–C₂₀)cycloalkyl-(C₁–C₁₉)heteroalkylene, (C₂–C₁₉)heterocycloalkyl-

(C₁–C₂₀)heteroalkylene, (C₁–C₅₀)heteroaryl, (C₁–C₁₉)heteroaryl-(C₁–C₂₀)alkylene, (C₆–C₂₀)aryl-(C₁–C₁₉)heteroalkylene, or (C₁–C₁₉)heteroaryl-(C₁–C₂₀)heteroalkylene.

[0046] The term “(C₄–C₅₀)heteroaryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi-, or tricyclic heteroaromatic hydrocarbon radical of from 4 to 50 total carbon atoms and from 1 to 10 heteroatoms. A monocyclic heteroaromatic hydrocarbon radical includes one heteroaromatic ring; a bicyclic heteroaromatic hydrocarbon radical has two rings; and a tricyclic heteroaromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic heteroaromatic hydrocarbon radical is present, at least one of the rings in the radical is heteroaromatic. The other ring or rings of the heteroaromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Other heteroaryl groups (e.g., (C_x–C_y)heteroaryl generally, such as (C₄–C₁₂)heteroaryl) are defined in an analogous manner as having from x to y carbon atoms (such as 4 to 12 carbon atoms) and being unsubstituted or substituted by one or more than one R^S. The monocyclic heteroaromatic hydrocarbon radical is a 5-membered ring or a 6-membered ring. The 5-membered ring has 5 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1, 2, 3, or 4; and each heteroatom may be O, S, N, or P.

[0047] The term “(C₁–C₅₀)heteroalkyl” means a saturated straight or branched chain radicals containing one to fifty carbon atoms, or fewer carbon atoms and one or more of the heteroatoms. The term “(C₁–C₅₀)heteroalkylene” means a saturated straight or branched chain diradicals containing from 1 to 50 carbon atoms and one or more than one heteroatoms. The heteroatoms of the heteroalkyls or the heteroalkylenes may include Si(R^C)₃, Ge(R^C)₃, Si(R^C)₂, Ge(R^C)₂, P(R^P)₂, P(R^P), N(R^N)₂, N(R^N), N, O, OR^C, S, SR^C, S(O), and S(O)₂, wherein each of the heteroalkyl and heteroalkylene groups are unsubstituted or are substituted by one or more R^S.

[0048] 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 the anionic form of the halogen atom: fluoride (F[–]), chloride (Cl[–]), bromide (Br[–]), or iodide (I[–]).

[0049] 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 and/or triple bonds optionally may or may not be

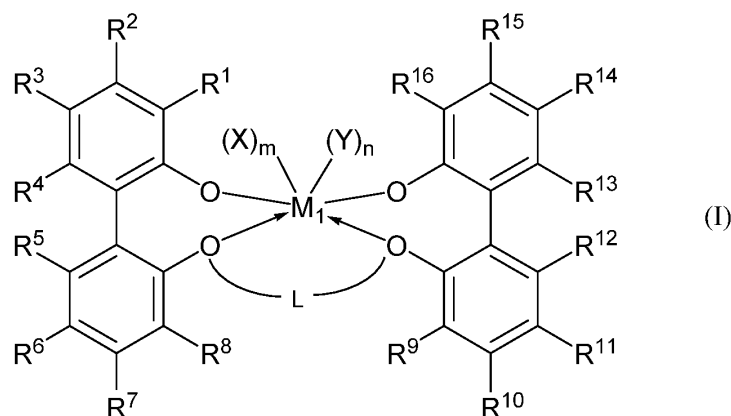
present in substituents R^S . The term “unsaturated” means containing one or more carbon–carbon double bonds, carbon–carbon triple bonds, or (in heteroatom-containing groups) one or more carbon–nitrogen, carbon–phosphorous, or carbon–silicon double bonds, not including double bonds that may be present in substituents R^S , if any, or in (hetero) aromatic rings, if any.

[0050] Embodiments of this disclosure include processes of polymerizing olefin monomers to produce polyolefin. The process includes reacting ethylene and optionally one or more olefin monomers in one reactor or multiple reactors in the presence of a catalyst system. The catalyst includes two or more catalysts, at least one of which is derived from bis-phenylphenoxy procatalysts according to formula (I) and at least one of which is derived from phosphinimine procatalyst according to formula (V). The amount of hydrogen gas is adjusted to tailor the molecular weight of the polyolefin.

[0051] The hydrogen gas may be added to the polymerization process. The amount of hydrogen gas may be 0 mmol in the reactor at any given time during the polymerization reaction. The amount of hydrogen may be increased or it may be decreased as the reaction progresses. In a semi-batch polymerization process the amount of hydrogen may decrease when the polymerization reactants consume the hydrogen gas and additional hydrogen gas is not added.

[0052] The catalyst comprises one or more bis-phenylphenoxy procatalysts according to formula (I) and one or more phosphinimine procatalysts according to formula (V).

[0053] Embodiments of this disclosure include catalyst systems that include one or more bis-phenylphenoxy procatalysts according to formula (I):



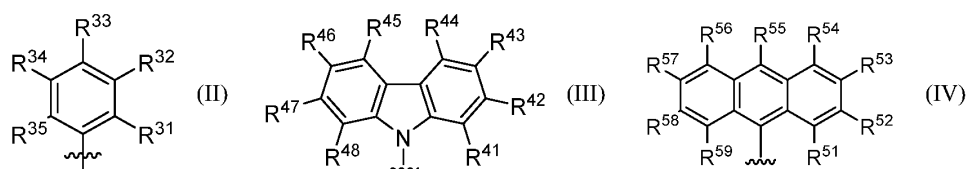
[0054] In formula (I), M_1 is titanium, zirconium, hafnium, scandium, or yttrium.

[0055] In formula (I), each X is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_3-Q(OR^C)_Q$, $-Si(R^C)_3-Q(OR^C)_Q$, $-OSi(R^C)_3-Q(OR^C)_Q$, $-CH_2Ge(R^C)_3-Q(OR^C)_Q$, $-Ge(R^C)_3-Q(OR^C)_Q$, $-P(R^C)_2-W(OR^C)_W$, $-P(O)(R^C)_2-W(OR^C)_W$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^CSi(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$, $-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$, $-NHC(O)R^C$, $-C(O)N(R^C)_2$, $-C(O)NHR^C$, $-C(O)NH_2$, 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 two X ligands can be connected to form a metallocycle ring.

[0056] In formulas (I), each Y is independently Lewis Base; optionally, X and Y can be linked to form a ring. Subscript m is 1 or 2; and subscript n is 0, 1 and 2.

[0057] 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.

[0058] 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, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N=C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



[0059] In formula (II), R^{31} , R^{32} , R^{33} , R^{34} , R^{35} are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$,

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

[0060] In formula (III), $\text{R}^{41}, \text{R}^{42}, \text{R}^{43}, \text{R}^{44}, \text{R}^{45}, \text{R}^{46}, \text{R}^{47}, \text{R}^{48}$ are independently chosen from $-\text{H}, (\text{C}_1-\text{C}_{50})\text{hydrocarbyl}, (\text{C}_1-\text{C}_{50})\text{heterohydrocarbyl}, -\text{Si}(\text{R}^{\text{C}})_3, -\text{Ge}(\text{R}^{\text{C}})_3, -\text{P}(\text{R}^{\text{P}})_2, -\text{N}(\text{R}^{\text{N}})_2, -\text{OR}^{\text{C}}, -\text{SR}^{\text{C}}, -\text{NO}_2, -\text{CN}, -\text{CF}_3, \text{R}^{\text{C}}\text{S}(\text{O})-, \text{R}^{\text{C}}\text{S}(\text{O})_2-, (\text{R}^{\text{C}})_2\text{C}=\text{N}-, \text{R}^{\text{C}}\text{C}(\text{O})\text{O}-, \text{R}^{\text{C}}\text{OC}(\text{O})-, \text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-, (\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen.

[0061] In formula (IV), $\text{R}^{51}, \text{R}^{52}, \text{R}^{53}, \text{R}^{54}, \text{R}^{55}, \text{R}^{56}, \text{R}^{57}, \text{R}^{58}$, and R^{59} are independently chosen from $-\text{H}, (\text{C}_1-\text{C}_{50})\text{hydrocarbyl}, (\text{C}_1-\text{C}_{50})\text{heterohydrocarbyl}, -\text{Si}(\text{R}^{\text{C}})_3, -\text{Ge}(\text{R}^{\text{C}})_3, -\text{P}(\text{R}^{\text{P}})_2, -\text{N}(\text{R}^{\text{N}})_2, -\text{OR}^{\text{C}}, -\text{SR}^{\text{C}}, -\text{NO}_2, -\text{CN}, -\text{CF}_3, \text{R}^{\text{C}}\text{S}(\text{O})-, \text{R}^{\text{C}}\text{S}(\text{O})_2-, (\text{R}^{\text{C}})_2\text{C}=\text{N}-, \text{R}^{\text{C}}\text{C}(\text{O})\text{O}-, \text{R}^{\text{C}}\text{OC}(\text{O})-, \text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-, (\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen.

[0062] The groups R^1 and R^{16} in the metal-ligand complex of formula (I) are chosen independently of one another. For example, R^1 may be chosen from a radical having formula (II), (III), or (IV), and R^{16} may be a $(\text{C}_4-\text{C}_{50})\text{heteroaryl}$; or R^1 may be chosen from a radical having formula (II), (III), or (IV), and R^{16} may be chosen from a radical having formula (II), (III), or (IV), the same as or different from that of R^1 . In embodiments, both R^1 and R^{16} are radicals having formula (II), for which the groups R^{31-35} are the same or different in R^1 and R^{16} . In some embodiments, both R^1 and R^{16} are radicals having formula (III), for which the groups R^{41-48} are the same or different in R^1 and R^{16} . In other embodiments, both R^1 and R^{16} are radicals having formula (IV), for which the groups R^{51-59} are the same or different in R^1 and R^{16} .

[0063] In embodiments, at least one of R^1 and R^{16} is a radical having formula (II), where at least one of R^{32} and R^{34} are *tert*-butyl. 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 $\text{R}^{41-42}, \text{R}^{44-45}$, and R^{47-48} are $-\text{H}$. In other embodiments, one of or both of R^{42} and R^{47} is *tert*-butyl and $\text{R}^{41}, \text{R}^{43-46}$, and R^{48} are $-\text{H}$. In some embodiments, both R^{42} and R^{47} are $-\text{H}$. In some embodiments, R^{41-48} are $-\text{H}$.

[0064] In formula (I), $\text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8, \text{R}^9, \text{R}^{10}, \text{R}^{11}, \text{R}^{12}, \text{R}^{13}, \text{R}^{14}$, and R^{15} are independently chosen from $-\text{H}, (\text{C}_1-\text{C}_{50})\text{hydrocarbyl}, (\text{C}_1-\text{C}_{50})\text{heterohydrocarbyl}, -\text{Si}(\text{R}^{\text{C}})_3, -\text{Ge}(\text{R}^{\text{C}})_3, -\text{P}(\text{R}^{\text{P}})_2, -\text{N}(\text{R}^{\text{N}})_2, -\text{OR}^{\text{C}}, -\text{SR}^{\text{C}}, -\text{NO}_2, -\text{CN}, -\text{CF}_3, \text{R}^{\text{C}}\text{S}(\text{O})-, \text{R}^{\text{C}}\text{S}(\text{O})_2-, (\text{R}^{\text{C}})_2\text{C}=\text{N}-, \text{R}^{\text{C}}\text{C}(\text{O})\text{O}-, \text{R}^{\text{C}}\text{OC}(\text{O})-, \text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-, (\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, and halogen.

[0065] In some embodiments, at least one of $\text{R}^5, \text{R}^6, \text{R}^7$, and R^8 is a halogen atom; and at least one of $\text{R}^9, \text{R}^{10}, \text{R}^{11}$, and R^{12} is a halogen atom. In some embodiments, at least two of R^5 ,

R^6 , R^7 , and R^8 are halogen atoms; and at least two of R^9 , R^{10} , R^{11} , and R^{12} are halogen atoms. In various embodiments, at least three of R^5 , R^6 , R^7 , and R^8 are halogen atoms; and at least three of R^9 , R^{10} , R^{11} , and R^{12} are halogen atoms.

[0066] In embodiments, R^3 and R^{14} are (C_1-C_{24}) alkyl. In various embodiments, R^3 and R^{14} are (C_1-C_{20}) alkyl. In some embodiments, R^3 and R^{14} are (C_4-C_{24}) alkyl. In one or more embodiments, R^3 and R^{14} are (C_8-C_{12}) 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.

[0067] In embodiments, R^3 and R^{14} are methyl. In other 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.

[0068] In some embodiments, R^6 and R^{11} are halogen. In other embodiments, R^6 and R^{11} are (C_1-C_{24}) alkyl. In some 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.

[0069] In some embodiments, R^3 and R^{14} are methyl and R^6 and R^{11} are halogen. In other embodiments, R^6 and R^{11} are *tert*-butyl. In other embodiments, R^3 and R^{14} are *tert*-octyl or *n*-octyl.

[0070] In one or more embodiments, in formula (I), at least one of R^1 and R^{16} is a radical having formula (III). In some embodiments, when one of R^1 and R^{16} is a radical having formula

(III) R^{42} and R^{47} are (C_1-C_{20}) hydrocarbyl or $-\text{Si}[(C_1-C_{20})\text{hydrocarbyl}]_3$. In various embodiments, when one of R^1 and R^{16} is a radical having formula (III), R^{43} and R^{46} are (C_1-C_{20}) hydrocarbyl or $-\text{Si}[(C_1-C_{20})\text{hydrocarbyl}]_3$.

[0071] In some embodiments, in formula (I), at least one of R^1 and R^{16} is a radical having formula (II) and R^{32} and R^{34} are (C_1-C_{12}) hydrocarbyl or $-\text{Si}[(C_1-C_{20})\text{hydrocarbyl}]_3$.

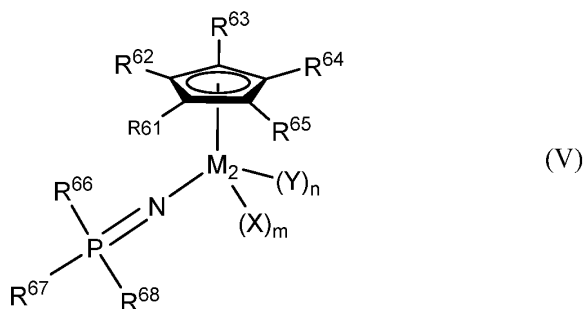
[0072] In various embodiments, in formula (I), at least one of R^1 and R^{16} is a radical having formula (IV) and at least two of R^{52} , R^{53} , R^{55} , R^{57} , and R^{58} are (C_1-C_{20}) hydrocarbyl or $-\text{Si}[(C_1-C_{20})\text{hydrocarbyl}]_3$.

[0073] In one or more embodiments, R^8 and R^9 are independently (C_1-C_4) alkyl.

[0074] In some embodiments, R^3 and R^{14} are (C_1-C_{20}) alkyl. In various embodiments, R^3 and R^{14} are methyl, R^6 and R^{11} are halogen. In one or more embodiments, R^6 and R^{11} are *tert*-butyl. In some embodiments, R^3 and R^{14} are *tert*-octyl or *n*-octyl.

[0075] In some embodiments, L is chosen from $-\text{CH}_2(\text{CH}_2)_m\text{CH}_2-$, $-\text{CH}_2\text{Si}(\text{R}^C)(\text{R}^D)\text{CH}_2-$, $-\text{CH}_2\text{Ge}(\text{R}^C)(\text{R}^D)\text{CH}_2-$, $-\text{CH}_2(\text{CH}_3)\text{CH}_2\text{CH}^*(\text{CH}_3)$, bis(methylene)cyclohexan-1,2-diyl; $-\text{CH}_2\text{CH}(\text{R}^C)\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{R}^C)_2\text{CH}_2-$, where each R^C in L is (C_1-C_{20}) hydrocarbyl and R^D in L is (C_1-C_{20}) hydrocarbyl.

[0076] Embodiments of this disclosure include catalyst systems that include one or more phosphinimine procatalysts according to formula (V):



[0077] In formula (V), M_2 is titanium, zirconium, or hafnium.

[0078] In formula (V), each X is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-\text{CH}_2\text{Si}(\text{R}^C)_{3-Q}(\text{OR}^C)_Q$, $-\text{Si}(\text{R}^C)_{3-Q}(\text{OR}^C)_Q$, $-\text{OSi}(\text{R}^C)_{3-Q}(\text{OR}^C)_Q$, $-\text{CH}_2\text{Ge}(\text{R}^C)_{3-Q}(\text{OR}^C)_Q$, $-\text{Ge}(\text{R}^C)_{3-Q}(\text{OR}^C)_Q$, $-\text{P}(\text{R}^C)_{2-W}(\text{OR}^C)_W$, $-\text{P}(\text{O})(\text{R}^C)_{2-W}(\text{OR}^C)_W$, $-\text{N}(\text{R}^C)_2$, $-\text{NH}(\text{R}^C)$, $-\text{N}(\text{Si}(\text{R}^C)_3)_2$, $-\text{NR}^C\text{Si}(\text{R}^C)_3$, $-\text{NHSi}(\text{R}^C)_3$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $-\text{OCF}_3$, $-\text{S}(\text{O})\text{R}^C$, $-\text{S}(\text{O})_2\text{R}^C$, $-\text{OS}(\text{O})_2\text{R}^C$,

$-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $-\text{N}=\text{CH}(\text{R}^{\text{C}})$, $-\text{N}=\text{CH}_2$, $-\text{N}=\text{P}(\text{R}^{\text{C}})_3$, $-\text{OC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{OR}^{\text{C}}$, $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{R}^{\text{C}}$, $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{H}$, $-\text{NHC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{N}(\text{R}^{\text{C}})_2$, $-\text{C}(\text{O})\text{NHR}^{\text{C}}$, $-\text{C}(\text{O})\text{NH}_2$, 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 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, wherein two X ligands can be connected to form a metallacycle ring.

[0079] In formula (V), each Y is independently Lewis Base; optionally, X and Y can be linked to form a ring. Subscript m is 1 or 2; and subscript n is 0, 1 and 2.

[0080] In formula (V), R^{61} , R^{62} , R^{63} , R^{64} , and R^{65} are independently $(\text{C}_1-\text{C}_{50})$ hydrocarbyl, wherein R^{61} and R^{62} are optionally connected to form a ring, or R^{62} and R^{63} are optionally connected to form a ring, R^{63} and R^{64} are optionally connected to form a ring, R^{64} and R^{65} optionally are connected to form a ring;

[0081] In formula (V), R^{66} , R^{67} , and R^{68} are independently $(\text{C}_1-\text{C}_{20})$ hydrocarbyl, $(\text{C}_1-\text{C}_{20})$ heterohydrocarbyl, $(\text{C}_6-\text{C}_{30})$ aryl, $(\text{C}_5-\text{C}_{30})$ heteroaryl wherein two of R^{66} , R^{67} , and R^{68} are optionally connected to form a ring; and

[0082] In formulas (I), (II), (III), (IV), and (V), 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 $-\text{H}$.

[0083] In one or more embodiments, in formula (V), R^{66} , R^{67} , R^{68} are independently $(\text{C}_1-\text{C}_{20})$ alkyl.

[0084] In some embodiments, in formula (V), R^{66} , R^{67} , R^{68} 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, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0085] In various embodiments, in formula (V), wherein R^{64} and R^{65} are connected to form an aromatic ring.

[0086] In some embodiments, the monodentate ligand, X and Y of formula (I) and formula (V) may be a monoanionic ligand. Monoanionic ligands have a net formal oxidation state of -1 . Each monoanionic ligand may independently be hydride, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl carbanion, $(\text{C}_1-\text{C}_{40})$ heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, sulfate, $\text{HC}(\text{O})\text{O}^-$, $\text{HC}(\text{O})\text{N}(\text{H})^-$, $(\text{C}_1-\text{C}_{40})$ hydrocarbyl $\text{C}(\text{O})\text{O}^-$,

$(C_1-C_{40})\text{hydrocarbylC(O)N}((C_1-C_{20})\text{hydrocarbyl})^-$, $(C_1-C_{40})\text{hydrocarbylC(O)N(H)}^-$, $R^K R^L B^-$, $R^K R^L N^-$, $R^K O^-$, $R^K S^-$, $R^K R^L P^-$, or $R^M R^K R^L Si^-$, where each R^K , R^L , and R^M independently is hydrogen, $(C_1-C_{40})\text{hydrocarbyl}$, or $(C_1-C_{40})\text{heterohydrocarbyl}$, or R^K and R^L are taken together to form a $(C_2-C_{40})\text{hydrocarbylene}$ or $(C_1-C_{20})\text{heterohydrocarbylene}$ and R^M is as defined above.

[0087] In other embodiments, at least one monodentate ligand X and Y, independently from any other ligands X and other ligands Y, may be a neutral ligand. In specific embodiments, the neutral ligand is a neutral Lewis base group such as $R^Q NR^K R^L$, $R^K OR^L$, $R^K SR^L$, or $R^Q PR^K R^L$, where each R^Q independently is hydrogen, $[(C_1-C_{10})\text{hydrocarbyl}]_3 Si(C_1-C_{10})\text{hydrocarbyl}$, $(C_1-C_{40})\text{hydrocarbyl}$, $[(C_1-C_{10})\text{hydrocarbyl}]_3 Si$, or $(C_1-C_{40})\text{heterohydrocarbyl}$ and each R^K and R^L independently is as previously defined.

[0088] In the metal–ligand complex according to formula (I), each Y bonds with M 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, 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-butadiene.

[0089] In some embodiments, the Lewis base is an unsaturated $(C_1-C_{20})\text{hydrocarbon}$. In some embodiments, the Lewis base is cyclopentadiene or 1,3-butadiene. In various embodiments, the Lewis base is $(C_1-C_{20})\text{heterohydrocarbon}$, wherein the hetero atom of the heterohydrocarbon is oxygen. In some embodiments, Y is tetrahydrofuran, diethyl ether, or methyl *tert*-butyl ether (MTBE).

[0090] Additionally, each X and each Y can be a monodentate ligand that, independently from any other ligands X and Y, is a halogen, unsubstituted $(C_1-C_{20})\text{hydrocarbyl}$, unsubstituted $(C_1-C_{20})\text{hydrocarbylC(O)O-}$, or $R^K R^L N-$, wherein each of R^K and R^L independently is an unsubstituted $(C_1-C_{20})\text{hydrocarbyl}$. 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), and (V), X is benzyl, chloro, –CH₂SiMe₃, or phenyl.

[0091] In some embodiments, m + n is 2 or 3.

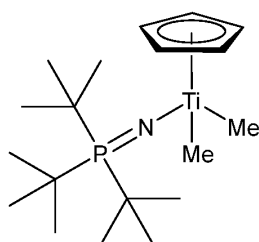
[0092] In further embodiments, each X and/or each Y is independently selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments, each X is the same. In other embodiments, at least two X are different from each other. In the embodiments, when m is 3 at least two X groups 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 X ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0093] In some embodiments, any or all of the chemical groups (e.g., X and R¹–R⁴) 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–R⁴ 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–R⁴ 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.

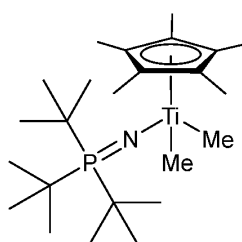
[0094] In some embodiments, the ratio of hydrogen chain transfer constants for the procatalyst of formula (V) to the procatalyst of formula (I) is greater than or equal to 3 at 160 °C. In other embodiments, the ratio of hydrogen chain transfer constants for the procatalyst of formula (V) to the procatalyst of formula (I) is greater than or equal to 5 at 160 °C; greater than or equal to 7 at 160 °C; or greater than or equal to 10 at 160 °C; or greater than or equal to 20 at 160 °C.

[0095] In illustrative embodiments, the catalyst systems may include a metal–ligand complex according to formula (I) having the structure of any of the Procatalysts BPP-1 to BPP-10 and metal–ligand complex according to formula (V) having the structure of any of procatalysts PN-1 to PN-3:

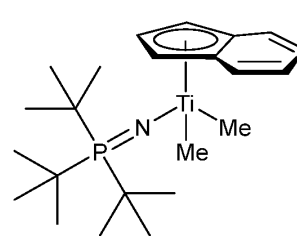
19



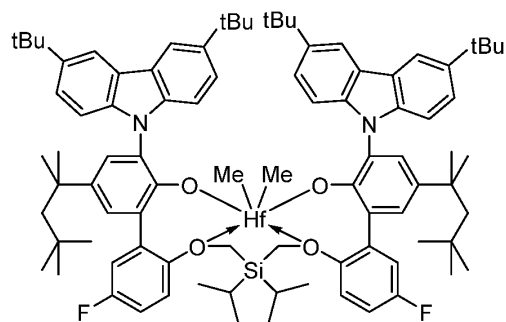
PN-1



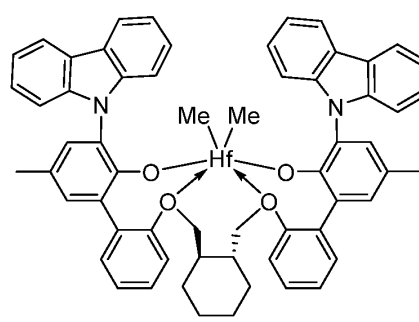
PN-2



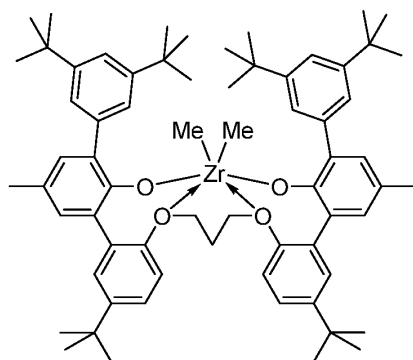
PN-3



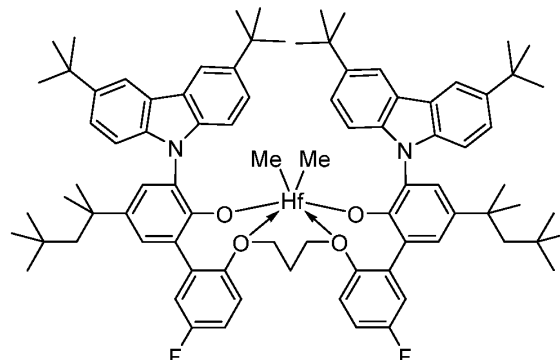
BPP-1



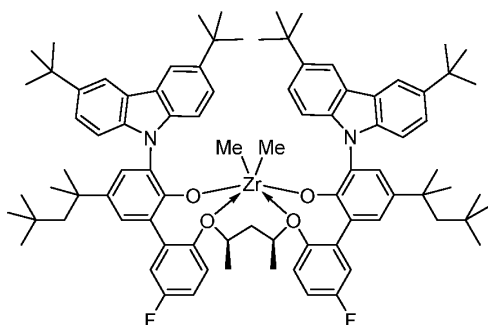
BPP-2



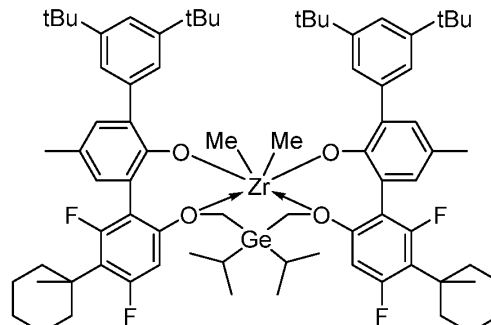
BPP-3



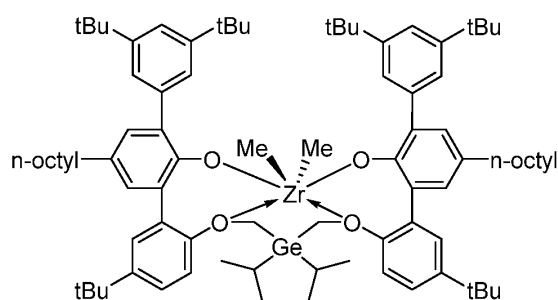
BPP-4



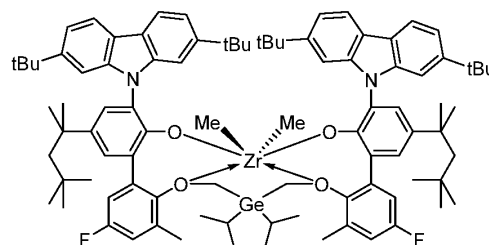
BPP-5



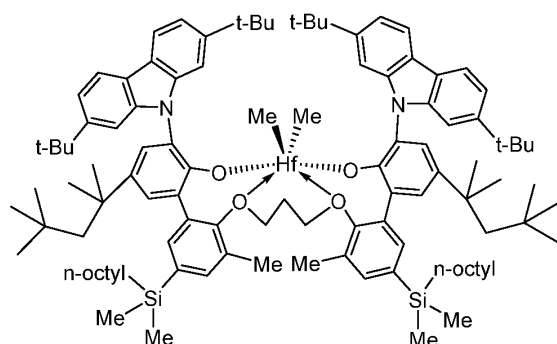
BPP-6



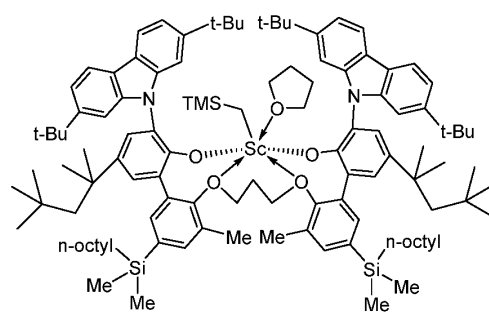
BPP-7



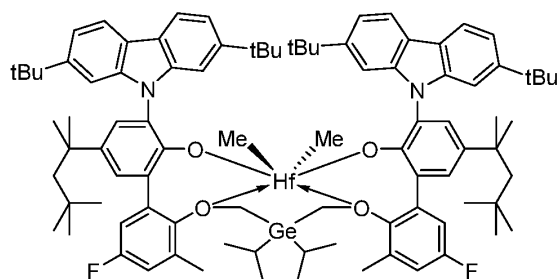
BPP-8



BPP-9



BPP-10



BPP-11

Cocatalyst Component

[0096] 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 precatalyst 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 precatalyst form, which is neutral, and a catalytic form, which may be positively charged due to the loss of a monoanionic ligand, such as 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.

[0097] 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 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.

[0098] A scavenging agent may sequester impurities in the reactor, and as such, may not constitute an activator. In some cases lower loading of alumoxanes do not act as co-catalysts, rather they serve as scavenging agent.

[0099] 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. 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.

[00100] Lewis acid activating co-catalysts include Group 13 metal compounds containing (C₁–C₂₀)hydrocarbyl substituents as described herein. In some embodiments, Group 13 metal

compounds are tri((C₁–C₂₀)hydrocarbyl)-substituted-aluminum or tri((C₁–C₂₀)hydrocarbyl)-boron compounds. In other embodiments, Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum, tri((C₁–C₂₀)hydrocarbyl)-boron compounds, tri((C₁–C₁₀)alkyl)aluminum, tri((C₆–C₁₈)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((C₁–C₂₀)hydrocarbyl borate (e.g. trityl tetrafluoroborate) or a tri((C₁–C₂₀)hydrocarbyl)ammonium tetra((C₁–C₂₀)hydrocarbyl)borane (e.g., bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁–C₂₀)hydrocarbyl)₄N⁺ a ((C₁–C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁–C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁–C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁–C₂₀)hydrocarbyl, when two or more are present, may be the same or different.

[00101] Combinations of neutral Lewis acid activating co-catalysts include mixtures comprising a combination of a tri((C₁–C₄)alkyl)aluminum and a halogenated tri((C₆–C₁₈)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-phenyl)borane): (alumoxane) [e.g., (Group 4 metal–ligand complex): (tris(pentafluoro-phenyl)borane): (alumoxane)] are from 1:1:1 to 1:10:30, in other embodiments, from 1:1:1.5 to 1:5:10.

[00102] The catalyst system that includes the metal–ligand complex of formula (I) 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 aluminosiloxanes, especially methyl aluminosiloxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to modified methyl aluminosiloxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1–) amine, and combinations thereof.

[00103] In some embodiments, more than one of the foregoing 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((C₁–C₄)hydrocarbyl)aluminum, tri((C₁–C₄)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 formula (I) 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, preferably the number of moles of the alumoxane that are employed is at least 100 times the number of moles of the metal–ligand complex of formula (I). 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 formula (I) 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 formula (I).

[00104] Polymerization Process

[00105] 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.

[00106] 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.

[00107] 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.

[00108] 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.

Polyolefins

[00109] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene and propylene. 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.

[00110] 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 percent by weight monomer units derived from ethylene. All individual values and subranges encompassed by “from at least 50 weight 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 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.

[00111] 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.

[00112] 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.

[00113] 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, gas phase polymerization processes, slurry phase polymerization processes, and combinations thereof using one or more conventional reactors

such as loop reactors, isothermal reactors, fluidized bed gas phase reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[00114] 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.

[00115] 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 cocatalysts, as described in the preceding paragraphs.

[00116] 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.

[00117] 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, wherein the catalyst system incorporates at least one metal–ligand complex of formula (I). 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 0.960 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.

[00118] In another embodiment, the polymer resulting from the catalyst system that includes the metal–ligand complex of formula (I) has a melt flow ratio (I_{10}/I_2) from 5 to 20, in which 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.

[00119] In some embodiments, the polymer resulting from the catalyst system that includes the metal–ligand complex of formula (I) 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.

[00120] Embodiments of the catalyst systems described in this disclosure yield unique polymer properties as a result of the high molecular weights of the polymers formed and the amount of the co-monomers incorporated into the polymers.

[00121] All solvents and reagents are obtained from commercial sources and used as received unless otherwise noted. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether are purified *via* passage through activated alumina and, in some cases, Q-5 reactant. Solvents used for experiments performed in a nitrogen-filled glovebox are further dried by storage over activated 4Å molecular sieves. Glassware for moisture-sensitive reactions is dried in an oven overnight prior to use. NMR spectra are recorded on Varian 400-MR and VNMR-

500 spectrometers. LC-MS analyses are performed using a Waters e2695 Separations Module coupled with a Waters 2424 ELS detector, a Waters 2998 PDA detector, and a Waters 3100 ESI mass detector. LC-MS separations are performed on an XBridge C18 3.5 μm 2.1x50 mm column using a 5:95 to 100:0 acetonitrile to water gradient with 0.1% formic acid as the ionizing agent. HRMS analyses are performed using an Agilent 1290 Infinity LC with a Zorbax Eclipse Plus C18 1.8 μm 2.1x50 mm column coupled with an Agilent 6230 TOF Mass Spectrometer with electrospray ionization. ^1H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet and m = multiplet), integration, and assignment). Chemical shifts for ^1H NMR data are reported in ppm downfield from internal tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent as references. ^{13}C NMR data are determined with ^1H decoupling, and the chemical shifts are reported downfield from tetramethylsilane (TMS, δ scale) in ppm versus the using residual carbons in the deuterated solvent as references.

Compositional Conventional GPC

[00122] 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. 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.

[00123] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 g/mol and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 °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 0.4315 and B is equal to 1.0.

[00124] 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.

[00125] 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.

[00126] 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.

[00127] 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.

$$\text{[00128]} \quad Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (\text{Equation 2})$$

$$[00129] \quad M_{W(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (\text{Equation 3})$$

$$[00130] \quad M_{Z(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (\text{Equation 4})$$

[00131] 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.

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

(Equation5)

Compositional Conventional UHMW GPC

[00132] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 165° Celsius and the column compartment and detectors were set at 155° Celsius. The columns used were 4 TOSOH TSKgel GMHHR-H (30) HT 30-micron particle size, mixed pore size columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00133] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 g/mol and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. Individually prepared polystyrene standards of 10,000,000 and 15,000,000 g/mol, both from Agilent Technologies, were also prepared, at 0.5 and 0.3 mg/mL respectively. 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)).

[00134] A third 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.

[00135] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 12,000 for the 4 TOSOH TSKgel GMHHR-H (30) HT 30-micron particle size, mixed pore size columns.

[00136] 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.

[00137] 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.

[00138] 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.

IR5 GPC Octene Composition Calibration

[00139] A calibration for the IR5 detector rationing was performed using at least ten ethylene-based polymer standards (Octene as comonomer) made by single-site metallocene catalyst from a single reactor in solution process (polyethylene homopolymer and ethylene/octene copolymers) of a narrow SCB distribution and known comonomer content (as measured by ¹³C NMR Method, Qiu et al., Anal. Chem.2009, 81, 8585–8589), ranging from homopolymer (0 SCB/1000 total C) to approximately 40 SCB/1000 total C, where total C = carbons in backbone + carbons in branches. Each standard had a weight-average molecular weight from 36,000 g/mole to 126,000 g/mole measured by GPC. Each standard had a molecular weight distribution (Mw/Mn) from 2.0 to 2.5. Polymer properties for the SCB standards are shown in Table A.

[00140] Table A: Copolymer Standards

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

14.3	0.2161	17.9	103,600	2.20
9.4	0.2031	11.8	103,200	2.26

[00141] The “IR5 Area Ratio (or “IR5 Methyl Channel Area / IR5 Measurement Channel Area”)” of “the baseline-subtracted area response of the IR5 methyl channel sensor” to “the baseline-subtracted area response of IR5 measurement channel sensor” (standard filters and filter wheel as supplied by PolymerChar: Part Number IR5_FWM01 included as part of the GPC-IR instrument) was calculated for each of the “Copolymer” standards. A linear fit of the Wt% Comonomer frequency versus the “IR5 Area Ratio” was constructed in the form of the following Equation 6:

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

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

Improved method for comonomer content analysis (iCCD)

[00142] (Cong and Parrott et al, W02017040127A1). iCCD test was performed with Crystallization Elution Fractionation instrumentation (CEF) (PolymerChar, Spain) equipped with IR-5 detector (PolymerChar, Spain) and two angle light scattering detector Model 2040 (Precision Detectors, currently Agilent Technologies). A guard column packed with 20-27 micron glass (MoSCi Corporation, USA) in a 5 cm or 10 cm (length)X1/4” (ID) stainless was installed just before IR- 5 detector in the detector oven. Ortho-dichlorobenzene (ODCB, 99% anhydrous grade or technical grade) was used. Silica gel 40 (particle size 0.2-0.5 mm, catalogue number 10181-3) from EMD Chemicals was obtained (can be used to dry ODCB solvent before). The CEF instrument is equipped with an autosampler with N₂ purging capability. ODCB is sparged with dried nitrogen (N₂) for one hour before use. Sample preparation was done with autosampler at 4 mg/ml (unless otherwise specified) under shaking at 160 °C for 1 hour. The injection volume was 300pl. The temperature profile of iCCD was: crystallization at 3 °C/min from 105 °C to 30 °C, the thermal equilibrium at 30 °C for 2 minute (including Soluble Fraction Elution Time being set as 2 minutes), elution at 3 °C/min from 30 °C to 140

°C. The flow rate during crystallization is 0.0 ml/min. The flow rate during elution is 0.50 ml/min. The data was collected at one data point/second.

[00143] The iCCD column was packed with gold coated nickel particles (Bright 7GNM8-NiS, Nippon Chemical Industrial Co.) in a 15cm (length)X1/4" (ID) stainless tubing. The column packing and conditioning were with a slurry method according to the reference (Cong, R.; Parrott, A.; Hollis, C.; Cheatham, M. W02017040127A1). The final pressure with TCB slurry packing was 150 Bars.

[00144] Column temperature calibration was performed by using a mixture of the Reference Material Linear homopolymer polyethylene (having zero comonomer content, Melt index (I2) of 1.0, polydispersity M_w/M_n approximately 2.6 by conventional gel permeation chromatography, 1.0mg/ml) and Eicosane (2mg/ml) in ODCB. iCCD temperature calibration consisted of four steps: (1) Calculating the delay volume defined as the temperature offset between the measured peak elution temperature of Eicosane minus 30.00 °C; (2) Subtracting the temperature offset of the elution temperature from iCCD raw temperature data. It is noted that this temperature offset is a function of experimental conditions, such as elution temperature, elution flow rate, etc.; (3) Creating a linear calibration line transforming the elution temperature across a range of 30.00 °C and 140.00 °C so that the linear homopolymer polyethylene reference had a peak temperature at 101.0 °C, and Eicosane had a peak temperature of 30.0 °C; (4) For the soluble fraction measured isothermally at 30 °C, the elution temperature below 30.0 °C is extrapolated linearly by using the elution heating rate of 3 °C/min according to the reference (Cerk and Cong et al., US9,688,795).

[00145] The comonomer content versus elution temperature of iCCD was constructed by using 12 reference materials (ethylene homopolymer and ethylene-octene random copolymer made with single site metallocene catalyst, having ethylene equivalent weight average molecular weight ranging from 35,000 to 128,000). All of these reference materials were analyzed same way as specified previously at 4 mg/mL. The reported elution peak temperatures were linearly fit to the linear equation $y = -6.3515x + 101.00$, where y represented elution temperature of iCCD and x represented the octene mole%, and R^2 was 0.978.

[00146] Molecular weight of polymer and the molecular weight of the polymer fractions was determined directly from LS detector (90 degree angle) and concentration detector (IR-5) according Rayleigh-Gans-Debys approximation (Striegel and Yau, Modern Size Exclusion

Liquid Chromatogram, Page 242 and Page 263) by assuming the form factor of 1 and all the virial coefficients equal to zero. Integration windows are set to integrate all the chromatograms in the elution temperature (temperature calibration is specified above) range from 23.0 to 120 °C.

[00147] The calculation of Molecular Weight (Mw) from iCCD includes the following four steps:

[00148] (1) Measuring the interdetector offset. The offset is defined as the geometric volume offset between LS with respect to concentration detector. It is calculated as the difference in the elution volume (mL) of polymer peak between concentration detector and LS chromatograms. It is converted to the temperature offset by using elution thermal rate and elution flow rate. A linear high density polyethylene (having zero comonomer content, Melt index (I2) of 1.0, polydispersity M_w/M_n approximately 2.6 by conventional gel permeation chromatography) is used. Same experimental conditions as the normal iCCD method above are used except the following parameters: crystallization at 10 °C/min from 140 °C to 137 °C, the thermal equilibrium at 137 °C for 1 minute as Soluble Fraction Elution Time, soluble fraction (SF) time of 7 minutes, elution at 3 °C/min from 137 °C to 142 °C. The flow rate during crystallization is 0.0 ml/min. The flow rate during elution is 0.80 ml/min. Sample concentration is 1.0 mg/ml.

[00149] (2) Each LS datapoint in LS chromatogram is shifted to correct for the interdetector offset before integration.

[00150] (3) Baseline subtracted LS and concentration chromatograms are integrated for the whole eluting temperature range of the Step (1). The MW detector constant is calculated by using a known MW HDPE sample in the range of 100,000 to 140,000Mw and the area ratio of the LS and concentration integrated signals. **[00218]** (4) Mw of the polymer was calculated by using the ratio of integrated light scattering detector (90 degree angle) to the concentration detector and using the MW detector constant.

[00151] Calculation of half width is defined as the temperature difference between the front temperature and the rear temperature at the half of the maximum peak height, the front temperature at the half of the maximum peak is searched forward from 35.0 °C., while the rear temperature at the half of the maximum peak is searched backward from 119.0 °C.

Chain transfer constant calculations

[00152] Chain transfer constant were calculated using the version of the Mayo equation shown in Equation 7 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 7 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.

$$\frac{1}{Mn} = \frac{1}{Mn_0} + c_{CTH} \frac{[H_2]}{28 \times [ethylene]} \quad \text{Equation 7}$$

Batch Reactor Polymerization Procedure

[00153] 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.

Procedure for Polymerization in Continuous Reactor A

[00154] 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. Hydrogen is supplied in pressurized cylinders as a high purity grade and is not further purified. The reactor monomer feed (ethylene) stream is pressurized via mechanical compressor to above reaction pressure at 525 psig. The solvent and comonomer (1-octene) feed are pressurized via a mechanical positive displacement pump to above reaction pressure at 525 psig. MMAO-3A, commercially available from Nouryon, was used as an impurity scavenger. The individual catalyst components (procatalyst or cocatalyst) were manually batch diluted to specified component concentrations with purified solvent (Isopar E) and pressured to above reaction pressure at 525 psig. The cocatalyst is $[\text{HNMe}(\text{C}_{18}\text{H}_{37})]_2[\text{B}(\text{C}_6\text{F}_5)_4]$, commercially available from Boulder Scientific, and was used at a 1.2 molar ratio relative to the metal-ligand complex of formula (I), formula (V), or to the total of both complexes of formula (I) and formula (V). All reaction feed flows were measured with mass flow meters and independently controlled with computer automated valve control systems.

[00155] The continuous solution polymerizations were carried out in one or more of a 5 liter (L) continuously stirred-tank reactor (CSTR), a 5.7 L CSTR, and/or a plug flow reactor. The CSTR reactors have independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The plug flow reactor has independent control of catalyst component feeds. The combined solvent, monomer, comonomer and hydrogen feed to the reactors is temperature controlled to anywhere between 5 °C to 50 °C and typically 25 °C. The fresh comonomer feed to the polymerization reactor is fed in with the solvent feed. The fresh solvent feed is controlled typically with each injector receiving half of the total fresh feed mass flow. The cocatalyst is fed based on a calculated specified molar ratio (1.2 molar equivalents) to the procatalysts. Immediately following each fresh injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The effluent from the polymerization reactor system (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits and passes through a control valve (responsible for maintaining the pressure of the reactor system at a specified target). As the stream exits the reactor it is contacted with water to stop the reaction. In addition, various additives, such as antioxidants, could be added at this point. The stream then goes through another set of static mixing elements to evenly disperse the catalyst kill and additives.

[00156] 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 reaction components. The stream then entered a two-stage separation and devolatilization system where the polymer was removed from the solvent, hydrogen, and unreacted monomer and comonomer. The separated and devolatilized polymer melt was pumped through a die specially designed for underwater pelletization, cut into uniform solid pellets, dried, and transferred into a box for storage.

Procedure for Polymerization in Continuous Reactor B

[00157] Raw materials (ethylene, 1-octene, 1-hexene) and the process solvent (a narrow boiling range high-purity isoparaffinic solvent Isopar-ETM, 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 via mechanical compressor to above reaction pressure at 725 psig. The solvent and comonomer (1-hexene or 1-octene) feed is pressurized via mechanical positive displacement pump to above reaction pressure at 725 psig. MMAO-3A, commercially available from AkzoNobel, was used as an impurity scavenger. The individual catalyst components (procatalyst cocatalyst) were manually batch diluted to specified component concentrations with purified solvent (Isopar E) and pressured to above reaction pressure at 725 psig. The cocatalyst is [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄], commercially available from Boulder Scientific, and was used at a 1.2 molar ratio relative to the procatalysts. All reaction feed flows are measured with mass flow meters and independently controlled with computer automated valve control systems.

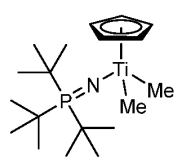
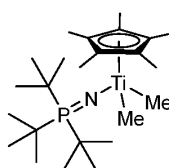
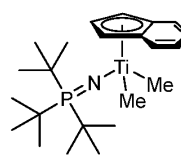
[00158] The continuous solution polymerizations are carried out in a 5 liters (L) continuously stirred-tank reactor (CSTR). The reactor has independent control of all fresh solvent, monomer, comonomer, hydrogen, and catalyst component feeds. The combined solvent, monomer, comonomer and hydrogen feed to the reactor is temperature controlled to anywhere between 5 °C to 50 °C and typically 25 °C. The fresh comonomer feed to the polymerization reactor is fed in with the solvent feed. The fresh solvent feed is controlled typically with each injector receiving half of the total fresh feed mass flow. The co-catalyst is fed based on a calculated specified molar ratio (1.2 molar equivalents) to the procatalyst components. Immediately following each fresh injection location, the feed streams are mixed with the circulating polymerization reactor contents with static mixing elements. The effluent

from the polymerization reactor (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) exits the first reactor loop and passes through a control valve (responsible for maintaining the pressure of the reactor at a specified target). As the stream exits the reactor it is contacted with water to stop the reaction. In addition, various additives such as antioxidants, can be added at this point. The stream then goes through another set of static mixing elements to evenly disperse the catalyst kill and additives.

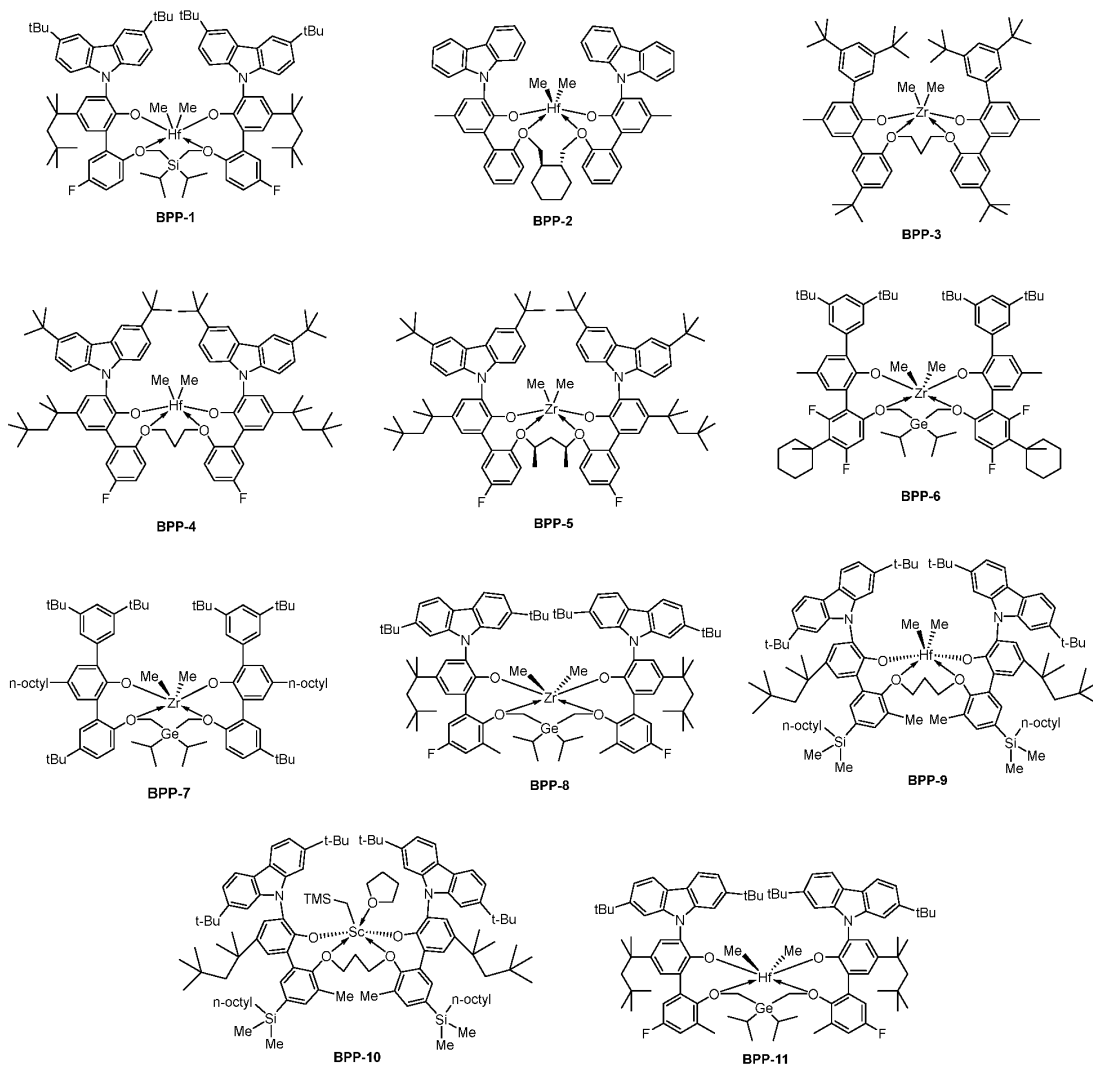
[00159] Following additive addition, the effluent (containing solvent, monomer, comonomer, hydrogen, catalyst components, and molten polymer) passed through a heat exchanger to raise the stream temperature in preparation for separation of the polymer from the other lower boiling reaction components. The stream then enters a two-stage separation and devolatilization system where the polymer is removed from the solvent, hydrogen, and unreacted monomer and comonomer. The separated and devolatilized polymer melt is pumped to a devolatilizing extruder. The polymer strand exits the extruder and enters a chilled water bath where the polymer crystallizes before entering a strand chopper for granulation.

EXAMPLES

[00160] The results of the polymerization reactions of Procatalysts PN-1, PN-2, or PN-3 in combination with BPP-1, BPP-2, BPP-3, BPP-4 BPP-5, BPP-6, BPP-7, BPP-8, BPP-9, or BPP-10 are tabulated and discussed. One or more features of the present disclosure are illustrated in view of the examples as follows:

**PN-1****PN-2****PN-3**

40



[00161] Polymerization conditions: 3.79L (1 Gal) batch reactor, 1250 g of Isopar-E; procatalyst:activator = 1:1.2; activator: $[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$; 50 equiv of MMAO-3A; 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.

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)
PN-1	522,700	47,210	19,560	10,340	5,430	2,970
PN-2	407,000	14,820	9,000	4,930	1,550	1,790
PN-3	403,900	27,770	16,010	9,200	5,610	3,670
BPP-1	892,900	664,800	509,600	485,900	--	--
BPP-2	928,400	694,600	565,300	361,000	263,700	142,800
BPP-3	459,600	361,700	277,100	203,600	129,500	76,400
BPP-4	557,100	--	--	407,100	--	--
BPP-6	1,291,000	--	--	219,800	--	--
BPP-7	1,695,000	473,600	444,900	264,400	--	--
BPP-9	693,600	610,600	547,100	451,500	354,100	146,000
BPP-10	232,000	183,100	162,200	104,700	68,600	40,800

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)
PN-1	261,600	42,200	18,500	10,800	6,100	3,200
PN-2	110,900	18,100	10,200	7,600	5,100	5,100
PN-3	124,300	31,500	16,900	9,200	5,600	3,700
BPP-1	559,500	538,200	482,500	408,500	--	--
BPP-2	356,200	263,800	178,700	163,000	100,100	47,700
BPP-3	289,000	218,400	186,600	140,000	94,400	63,000
BPP-4	276,300	--	--	247,900	--	--
BPP-6	612,300	--	--	142,000	--	--
BPP-7	570,000	439,200	303,100	179,700	--	--
BPP-8	--	496,000	416,700	254,300	189,100	94,600
BPP-9	414,500	380,100	344,100	290,600	211,500	154,300
BPP-11	1,500,800	--	--	593,900	--	--

Table 3: Polymer Composition Produced by PN-1 and BPP-1 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
C1	PN-1	5 mmol	28,100	56,800	111,900	2.0	4.0
C2	BPP-1	5 mmol	209,400	509,900	915,700	2.4	4.4
I1	PN-1/BPP-1	0 mmol	142,800	302,400	558,100	2.1	3.9
I2	PN-1/BPP-1	5 mmol	60,300	300,500	788,800	5.0	13.1
I3	PN-1/BPP-1	20 mmol	11,000	85,000	468,700	7.7	42.6
I4	PN-1/BPP-1	40 mmol	5,700	83,400	453,900	14.5	79.0

Table 4: Polymer Composition Produced by PN-1 and BPP-4 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
C3	PN-1	5 mmol	38,600	66,900	107,200	1.7	2.8
C4	BPP-4	5 mmol	261,200	496,000	839,600	1.9	3.2
I5	PN-1/BPP-4	0 mmol	268,500	485,800	801,700	1.8	3.0
I6	PN-1/BPP-4	5 mmol	46,500	122,300	350,200	2.6	7.5
I7	PN-1/BPP-4	20 mmol	13,200	63,500	375,500	4.8	28.5
I8	PN-1/BPP-4	40 mmol	6,640	94,900	499,300	14.3	75.2

Table 5: Polymer Composition Produced by PN-1 and BPP-5 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
C3	PN-1	5 mmol	38,600	66,900	107,200	1.7	2.8
C5	BPP-5	5 mmol	4,670	692,900	1,346,000	148.5	288.5
I9	PN-1/BPP-5	0 mmol	9,250	816,200	1,990,000	88.2	215.1
I10	PN-1/BPP-5	5 mmol	93,100	512,200	1,229,000	5.5	13.2
I11	PN-1/BPP-5	20 mmol	14,740	225,500	594,300	15.3	40.3
I12	PN-1/BPP-5	40 mmol	8,540	124,700	322,400	14.6	37.8

Table 6: Polymer Composition Produced by PN-1 and BPP-6 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
--	-------------	------------------	------------	------------	------------	-------	-------

C3	PN-1	5 mmol	38,600	66,900	107,200	1.7	2.8
C6	BPP-6	5 mmol	195,500	722,200	1,411,000	3.7	7.2
I13	PN-1/BPP-6	0 mmol	305,900	647,800	1,203,000	2.1	1.9
I14	PN-1/BPP-6	5 mmol	49,200	206,500	883,000	4.2	18.0
I15	PN-1/BPP-6	20 mmol	15,200	82,100	431,000	5.4	28.4
I16	PN-1/BPP-6	40 mmol	11,700	108,600	334,000	9.3	28.5

Table 7: Polymer Composition Produced by PN-1 and BPP-7 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
C3	PN-1	5 mmol	38,600	66,900	107,200	1.7	2.8
C7	BPP-7	5 mmol	193,300	661,100	1,378,000	3.4	7.1
I17	PN-1/BPP-7	0 mmol	361,100	1,016,000	2,205,000	2.2	6.1
I18	PN-1/BPP-7	5 mmol	40,500	210,500	977,000	5.2	24.1
I19	PN-1/BPP-7	20 mmol	27,000	254,400	687,500	9.4	25.5
I20	PN-1/BPP-7	40 mmol	16,900	165,800	386,400	9.8	22.9

Table 8: Polymer Composition Produced by PN-1 and BPP-8 at three different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mn
C8	PN-1	10 mmol	24,200	47,210	91,340	2.2	3.8
C9	BPP-8	10 mmol	101,200	589,700	1,267,000	5.8	12.5
I21	PN-1/BPP-8	10 mmol	23,070	243,900	1,090,000	7.1	19.1
I22	PN-1/BPP-8	20 mmol	34,380	418,600	931,800	12.2	27.1
I23	PN-1/BPP-8	40 mmol	19,800	241,700	556,800	12.2	28.1

Table 9: Polymer Composition Produced by PN-1 and BPP-8 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
C1	PN-1	5 mmol	28,100	56,800	111,900	2.0	4.0
C10	BPP-8	5 mmol	111,800	517,400	1,001,000	4.6	9.0
I24	PN-1/BPP-8	0 mmol	58,410	280,300	684,800	4.8	11.7
I25	PN-1/BPP-8	5 mmol	46,450	193,600	660,600	4.2	14.2
I26	PN-1/BPP-8	20 mmol	15,900	158,200	507,600	9.9	31.9
I27	PN-1/BPP-8	40 mmol	11,630	163,200	456,600	14.0	39.3

[00162] Some BPP catalysts have a larger Mz/Mn values such as in C9 and C10. For example, BPP-8 produces a polymer having a low molecular weight tail that leads to a larger Mz/Mn, as tabulated in C10. However, an increase in Mz/Mn over this starting value is still observed when this catalyst is combined with a PN catalyst shown in the results of I21 – I23 and I24 – I27.

Table 10: Polymer Composition Produced by PN-1 and BPP-9 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
C11	PN-1	5 mmol	32,940	73,180	119,100	2.2	3.6
C12	BPP-9	5 mmol	234,400	574,000	1,178,000	2.5	5.0
I28	PN-1/BPP-9	0 mmol	207,600	531,900	1,142,000	2.6	5.5
I29	PN-1/BPP-9	5 mmol	25,800	97,500	380,700	3.9	14.7
I30	PN-1/BPP-9	20 mmol	10,180	82,600	477,200	5.8	46.9
I31	PN-1/BPP-9	40 mmol	5,960	87,700	475,900	5.4	79.8

Table 11: Polymer Composition Produced by PN-1 and BPP-10 at two different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mn
C17	PN-1	5 mmol	32,940	73,180	119,100	2.2	3.6
C20	BPP-10	5 mmol	106,500	215,700	376,800	2.0	3.5
C21	PN-1/BPP-10	0 mmol	146,000	339,700	687,700	2.3	4.7
I25	PN-1/BPP-10	20 mmol	13,400	51,100	199,900	3.8	15.0

Table 12: Polymer Composition Produced by PN-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
C11	PN-3	5 mmol	22,550	55,400	118,900	2.5	5.2
C12	BPP-1	5 mmol	226,600	719,400	1,435,000	3.2	6.3
I32	PN-3/BPP-1	0 mmol	93,230	320,400	763,000	3.4	8.2
I33	PN-3/BPP-1	5 mmol	23,860	141,300	734,800	5.9	30.8
C11	PN-3/BPP-1	20 mmol	11,170	337,500	1,078,000	30.2	96.5
C12	PN-3/BPP-1	40 mmol	7,570	295,200	847,700	38.9	112.0

Table 13: Polymer Composition Produced by PN-3 and BPP-1 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
C15	PN-3	5 mmol	20,140	54,900	135,100	2.7	6.7
C2	BPP-1	5 mmol	209,400	509,900	915,700	2.4	4.4
I38	PN-3/BPP-1	0 mmol	74,900	220,200	479,000	2.9	6.4
I39	PN-3/BPP-1	5 mmol	24,340	129,400	514,700	5.3	21.1
I41	PN-3/BPP-1	20 mmol	8,460	183,600	656,300	21.7	77.6
I41	PN-3/BPP-1	40 mmol	7,920	236,300	609,500	29.9	77.0

Table 14: Polymer Composition Produced by PN-3 and BPP-7 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
--	-------------	------------------	------------	------------	------------	-------	-------

C13	PN-3	5 mmol	22,550	55,400	118,900	2.5	5.2
C14	BPP-7	5 mmol	193,300	661,100	1,378,000	3.4	7.1
I42	PN-3/BPP-7	0 mmol	106,900	446,800	1,636,000	4.2	15.3
I43	PN-3/BPP-7	5 mmol	30,940	194,600	877,100	6.2	28.3
I44	PN-3/BPP-7	20 mmol	11,620	194,600	598,500	16.8	51.5
I45	PN-3/BPP-7	40 mmol	8,140	139,200	366,600	17.1	45.1

Table 15 Polymer Composition Produced by PN-3 and BPP-7 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
C15	PN-3	5 mmol	20,140	54,900	135,100	2.7	6.7
C15	BPP-7	5 mmol	126,700	385,400	724,800	3.0	5.7
I46	PN-3/BPP-7	0 mmol	89,720	262,100	581,000	2.9	6.5
I47	PN-3/BPP-7	5 mmol	25,550	120,900	437,100	4.7	17.1
I48	PN-3/BPP-7	20 mmol	11,000	130,200	366,200	11.8	33.3
I49	PN-3/BPP-7	40 mmol	7,520	91,200	226,900	12.1	30.2

Table 16 Reactor and Feed Conditions to Produce Comparative Examples C16 – C21 and Inventive Examples I50 – I57

	C16	I50	C17	I51	C18	I52	C19	I53	C20	I54	I55	I56	C21	I57
Reactor Configuration	Singl e	Dual Paral lel	Singl e	Singl e	Dual Serie s	Dual Serie s	Dual Serie s	Dual Serie s	Singl e	Singl e	Singl e	Singl e	Singl e	Dual Serie s
Continuous Procedure	A	A	A	A	A	A	A	A	B	B	A	A	A	A
Comonomer Type	1-octen e	1-octen e	1-octen e	1-octen e	1-octen e	1-octen e	1-octen e	1-octen e	1-hexene	1-hexene	1-octen e	1-octen e	1-octen e	1-octen e
Catalyst 1	BPP-7	BPP-7	PN-1	PN-1	PN-1	PN-1	PN-1	PN-1	PN-1	PN-1	PN-1	PN-1	PN-1	BPP-11
Catalyst 1 Reactor	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1	Reac tor 1
Catalyst 2	--	PN-001	--	BPP-1	--	BPP-1	--	BPP-1	--	BPP-1	BPP-6	BPP-6	--	--
Catalyst 2 Reactor	--	Reac tor 2	--	Reac tor 1	--	Reac tor 2	--	Reac tor 2	--	Reac tor 1	Reac tor 1	Reac tor 1	--	Reac tor 2
Catalyst 1 Feed Con. (mmol/kg)	0.2	0.2	0.2	0.2	0.4	0.4	0.4	0.4	0.003	0.003	0.1	0.1	0.2	0.2
Catalyst 1 Flow (g/hr)	147.0	142.3	184.4	168.6	41.8	38.6	46.9	47.7	189.8	136.2	84.7	111.2	81.8	68.7
Reactor 1 [HNMe(C ₁₈ H ₃₇) ₂] [B(C ₆ F ₅) ₄] equiv	1.2	1.2	1.2	1.4	1.2	1.2	1.2	1.2	1.2	1.2	3.4	1.2	1.2	1.2
Reactor 1 MMAO-3A equiv	13.8	15.0	8.0	9.0	9.0	9.7	8.1	7.9	43	37	65.8	27.0	12.3	14.7
Catalyst 2 Feed Con. (mmol/kg)	--	0.2	--	0.08	--	0.15	--	0.15	--	0.002	0.03	0.03	--	152.8

Catalyst 2 Flow (g/hr)	--	100.8	--	88.7	--	299.8	--	259.5	--	93.0	220.7	137.5	--	0.1
Reactor 1 Type	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R	CST R
Reactor 1 Total Solvent Flow (kg/hr)	23.8	23.9	25.2	25.5	27.5	27.7	28.0	28.0	30.7	30.9	18.3	17.8	22.5	22.6
Reactor 1 Temp (°C)	160	160	190	190	190	190	190	190	186	186	150	150	180	180
Reactor 1 C2 Feed (kg/hr)	2.8	2.8	4.6	4.5	5.0	5.0	5.0	5.0	5.0	5.0	2.3	2.3	4.0	4.0
Reactor 1 C8 Feed (kg/hr)	1.5	1.5	0.54	0.55	1.7	1.7	1.2	1.2	3.0	3.1	0.08	0.4	3.2	3.0
Reactor 1 H2 Feed (sccm)	94.5	94.5	18.8	18.9	25.1	25.1	27.0	27.1	20.0	20.0	140.7	200	2.0	2.0
Reactor 1 H2 Feed (mol%)	0.25	0.25	0.031	0.031	0.038	0.038	0.04	0.04	0.065	0.065	0.46	0.66	0.004	0.004
Reactor 1 Exit [C2] (g/L)	12.0	12.5	3.0	3.0	12.0	12.0	10.0	10.0	18.0	17.8	10	10	12.1	13.0
Reactor 2 Type	--	CST R	--	--	Plug Flow	Plug Flow	Plug Flow	Plug Flow	--	--	--	--	--	Plug Flow
Reactor 2 Total Solvent Flow (kg/hr)	--	12.9	--	--	--	--	--	--	--	--	--	--	--	--
Reactor 2 Temp/Exit Temp (°C)	--	190	--	--	170	175	170	171	--	--	--	--	--	199
Reactor 2 C2 Feed (kg/hr)	--	2.3	--	--	--	--	--	--	--	--	--	--	--	--
Reactor 2 C8 Feed (kg/hr)	--	0.2	--	--	--	--	--	--	--	--	--	--	--	--
Reactor 2 H2 Feed (sccm)	--	11.0	--	--	--	--	--	--	--	--	--	--	--	--
Reactor 2 H2 Feed (mol%)	--	0.037	--	--	--	--	--	--	--	--	--	--	--	--
Reactor 2 Exit [C2] (g/L)	--	3.0	--	--	6.9	1.6	5.8	1.4	--	--	--	--	--	3.1

Table 17 Polymer Composition Produced by PN-1 and BPP-7, PN-1 and BPP-1, PN-1 and BPP-6, and PN-1 and BPP-11 in dual and single reactor setups.

	Catalyst(s)	I2 (dg/min)	I10/I2	Density (g/cc)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn	Mz/Mn
C16	BPP-7	0.6	5.7	0.9057	57,440	122,800	223,700	2.1	3.9
I50	BPP-7/PN-1	0.89	6.2	0.9185	38,230	105,600	202,400	2.8	5.3
C17	PN-1	6.8	6.3	0.9376	21,700	61,480	112,900	2.8	5.2

I51	PN-1/BPP-1	1.2	13.0	0.9366	25,910	113,700	704,500	4.4	27.2
C18	PN-1	2.7	6.2	0.9285	28,130	84,040	147,700	3.0	5.2
I52	PN-1/BPP-1	0.83	8.5	0.9204	31,880	116,000	323,400	3.6	10.1
C19	PN-1	3.0	6.1	0.9315	27,920	81,200	142,700	2.9	5.1
I53	PN-1/BPP-1	0.99	8.9	0.9260	35,810	101,000	268,700	2.8	7.5
C20	PN-1	2.7	6.9	0.9227	28,800	82,010	149,500	2.9	5.2
I54	PN-1/BPP-1	0.98	10.6	0.9161	33,510	145,200	610,100	4.3	18.2
I55	PN-1/BPP-6	0.12	11.2	0.9490	10,280	173,700	583,800	16.9	56.8
I56	PN-1/BPP-6	0.35	12.4	0.9385	8,590	135,000	512,200	15.7	59.6
C21	PN-1	2.5	14.4	0.9165	32,580	89,840	149,440	2.8	4.6
I57	PN-1/BPP-11	1.2	7.9	0.9185	37,260	108,380	250,380	2.9	6.7

Table 18: Constants for Chain Transfer to Hydrogen (cH₂) for Selected Catalysts at 160 °C

Catalyst	cH ₂
PN-1	0.534
PN-2	2.230
PN-3	1.268
BPP-1	0.011
BPP-2	0.008
BPP-3	0.012
BPP-9	0.036
BPP-10	0.016
BPP-11	0.0034*

*Calculated at 190 °C

[00163] FIG. 3 shows the GPC traces of the dual catalysts-produced polyethylene and PN-1 and BPP-1. As the amount of hydrogen gas increases, the molecular weight of the produced polyethylene separates into two distinct peaks. The changing the level of hydrogen significantly affects the molecular weight of the PN-produced PE, but the MW of the BPP-1-produced PE is largely unchanged. At 0 H₂, the molecular weights of the PN-1-produced PE at the BPP-1-produced PE are very similar and overlap. However, as the level of H₂ is increased from 5 mmol to 20 mmol and then to 40 mmol, the MW of the PN-1-produced PE drops significantly, while the MW of the BPP-1-produced PE remains largely unchanged, leading to the bimodality in the GPC traces in FIG. 3.

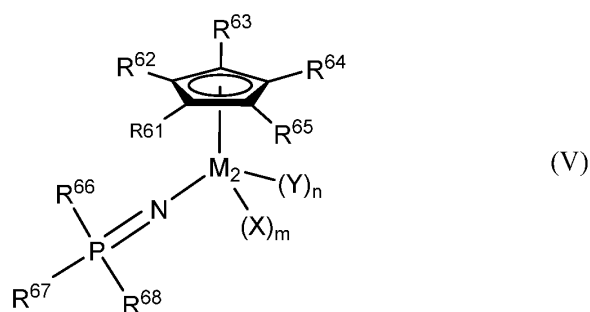
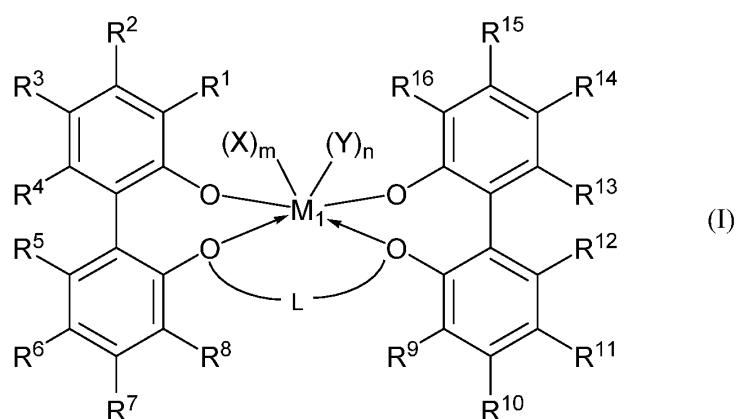
[00164] The inherent difference in comonomer incorporation between the PN-1 catalyst and the BPP-1 catalyst leads to a dual catalyst-produced resin that has a significant density split between the low molecular weight segment polyethylene and the higher molecular weight segment polyethylene, as shown in FIG. 4. The lower molecular weight segment polyethylene,

shown in FIG. 4, has a lower level of comonomer incorporation (~ 3 wt%) than does the high molecular weight segment polyethylene (~ 18 wt%) due to the different catalysts that produce each portion of the material.

[00165] FIG. 5 and FIG. 6 illustrate a similar behavior between other BPP catalysts and phosphinimine catalysts. For example, FIG. 5 and FIG. 6 show GPC data for the PN-1/BPP-2 catalyst pair. The GPC curves of these are analogous to the GPC data for the PN-1/BPP-1 catalyst pair shown above in FIG. 3 and FIG. 4. Here we see the same trend, where the molecular weight of the polymer produced by PN-1 and BPP-2 are similar with no hydrogen, but when hydrogen is introduced the molecular weight of the PN-1-produced polyethylene decreases significantly, while the molecular weight of the BPP-2-produced PE does not change much. FIGS. 8, 9, and 10 show similar trends.

CLAIMS

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



where, in formula (I):

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

each X is independently a monodentate ligand independently chosen from

(C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$,
 $-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, $-CH_2Ge(R^C)_{3-Q}(OR^C)_Q$,
 $-Ge(R^C)_{3-Q}(OR^C)_Q$, $-P(R^C)_{2-W}(OR^C)_W$, $-P(O)(R^C)_{2-W}(OR^C)_W$, $-N(R^C)_2$,
 $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^C Si(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$,

$-\text{CN}$, $-\text{CF}_3$, $-\text{OCF}_3$, $-\text{S}(\text{O})\text{R}^{\text{C}}$, $-\text{S}(\text{O})_2\text{R}^{\text{C}}$, $-\text{OS}(\text{O})_2\text{R}^{\text{C}}$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$,
 $-\text{N}=\text{CH}(\text{R}^{\text{C}})$, $-\text{N}=\text{CH}_2$, $-\text{N}=\text{P}(\text{R}^{\text{C}})_3$, $-\text{OC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{OR}^{\text{C}}$, $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{R}^{\text{C}}$,
 $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{H}$, $-\text{NHC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{N}(\text{R}^{\text{C}})_2$, $-\text{C}(\text{O})\text{NHR}^{\text{C}}$, $-\text{C}(\text{O})\text{NH}_2$, 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
 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, wherein two X ligands can be connected to form a
 metallacycle ring

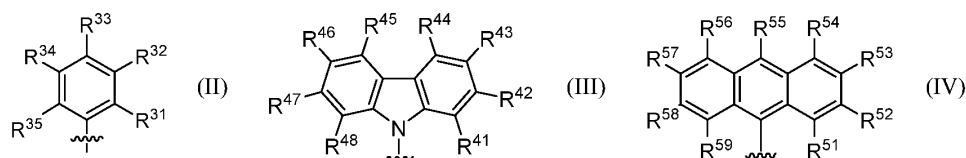
each Y is independently Lewis Base; optionally, X and Y can be linked to form a ring
 and a bidentate ligand.

m is 0, 1 or 2;

n is 0, 1 and 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, $-\text{Si}(\text{R}^{\text{C}})_3$,
 $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$,

$R^C S(O)_2-$, $(R^C)_2 C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2 NC(O)-$,
and halogen;

L is (C_1-C_{40}) hydrocarbylene or (C_2-C_{40}) heterohydrocarbylene; and
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 $-H$; and:

M_2 is titanium, zirconium, or hafnium;

R^{61} , R^{62} , R^{63} , R^{64} , and R^{65} are independently H, (C_1-C_{50}) hydrocarbyl,
 (C_1-C_{50}) heterohydrocarbyl wherein any of the R^{62} , R^{63} , R^{64} , and R^{65}
optionally are connected to form a ring or multi-ring structure;

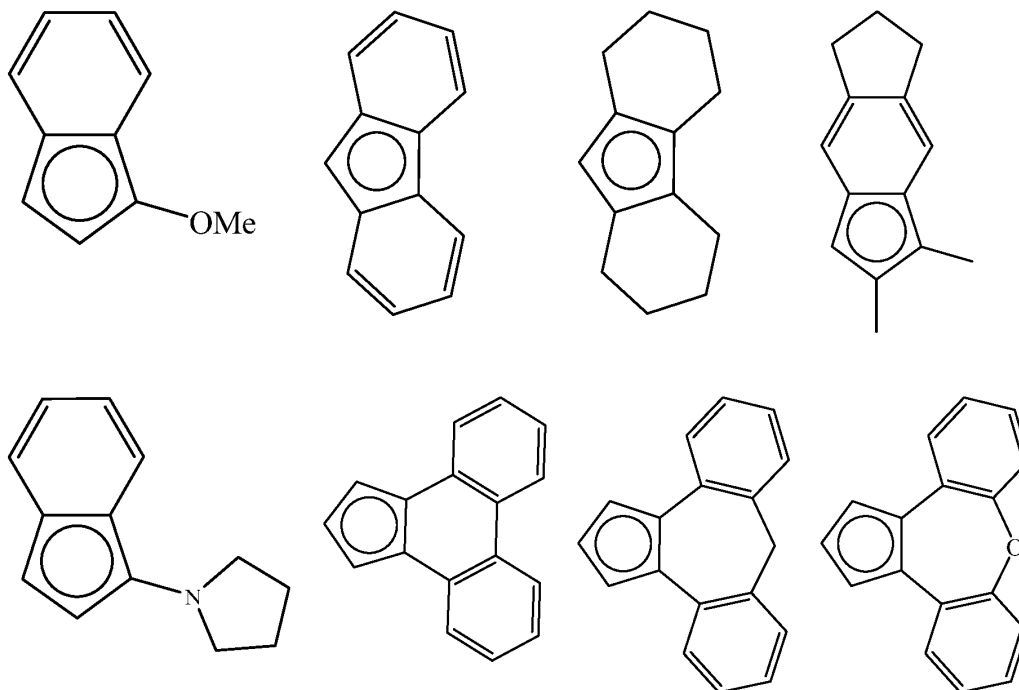
R^{66} , R^{67} , and R^{68} are independently (C_1-C_{20}) hydrocarbyl, (C_1-C_{20}) heterohydrocarbyl,
 (C_6-C_{30}) aryl, (C_5-C_{30}) heteroaryl wherein two of R^{66} , R^{67} , and R^{68} are
optionally connected to form a ring.

2. The polymerization process according to claim 1, wherein the ratio of hydrogen chain transfer constants for the procatalyst of formula (V) to the procatalyst of formula (I) is greater than or equal to 3 at 160 °C
3. The polymerization process according to claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (II).
4. The polymerization process according to claim 1, wherein at least one of R^1 and R^{16} is 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 of the preceding claims, wherein R^3 and R^{14} are *tert*-octyl or *n*-octyl.
8. The polymerization process according to any one of the preceding claims, wherein L is chosen from $-CH_2(CH_2)_mCH_2-$, $-CH_2Si(R^C)(R^D)CH_2-$, $-CH_2Ge(R^C)(R^D)CH_2-$,

$-\text{CH}_2(\text{CH}_3)\text{CH}_2\text{CH}^*(\text{CH}_3)$, bis(methylene)cyclohexan-1,2-diyl; $-\text{CH}_2\text{CH}(\text{R}^{\text{C}})\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{R}^{\text{C}})_2\text{CH}_2-$, where each R^{C} in L is $(\text{C}_1-\text{C}_{20})$ hydrocarbyl and R^{D} in L is $(\text{C}_1-\text{C}_{20})$ hydrocarbyl.

9. The polymerization process according to any one of the preceding claims, wherein R^{66} , R^{67} , R^{68} are independently $(\text{C}_1-\text{C}_{20})$ alkyl.
10. The polymerization process according to any one of the preceding claims, wherein R^{66} , R^{67} , R^{68} 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, 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 R^{61} , R^{62} , R^{63} , R^{64} , and R^{65} are H or (C_1-C_3) alkyl; or R^{61} , R^{62} , and R^{64} are (C_1-C_3) alkyl and R^{63} , R^{65} are H, or R^{61} and R^{63} are (C_1-C_3) alkyl and R^{62} , R^{64} , R^{65} are H.
12. The polymerization process according to any one of claims 1 to 11, wherein one of R^{61} , R^{62} , R^{63} , R^{64} , and R^{65} is selected from $-\text{OMe}$ and $-\text{NMe}_2$.
13. The polymerization process according to any one of claims 1 to 10, wherein:
 - (A) R^{61} and R^{62} are connected and form a ring and are optionally substituted by one or more R^{S} , wherein R^{S} is selected from the group consisting of $(\text{C}_1-\text{C}_{30})$ hydrocarbyl; or
 - (B) R^{63} and R^{64} are connected and form a ring and are optionally substituted by one or more R^{S} , wherein R^{S} is selected from the group consisting of $(\text{C}_1-\text{C}_{30})$ hydrocarbyl; or
 - (C) both (A) and (B);

wherein (A), (B), or (C) and the cyclopentadienyl of formula (V) have a structure selected from the group consisting of:



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