

BIDENTATE DIAZINYLAMIDO COMPLEXES AS CATALYSTS FOR OLEFIN POLYMERIZATION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/868,513, filed on June 28, 2019, the entire disclosure of which is hereby incorporated by reference.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to olefin polymerization catalyst systems and processes, and, more specifically, to olefin polymerization catalyst systems including bidentate diazinylamido Group IV transition metal catalysts and to olefin polymerization processes incorporating the catalyst systems.

BACKGROUND

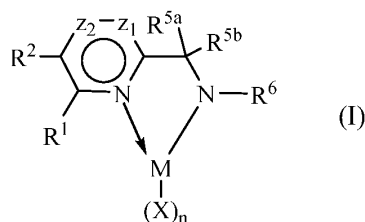
[0003] Olefin-based polymers such as polyethylene, ethylene-based polymers, polypropylene, and propylene-based polymers are produced via various catalyst systems. Selection of such catalyst systems used in the polymerization process of the olefin-based polymers is an important factor contributing to 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 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 high molecular weights and a narrow molecular weight distribution.

SUMMARY

[0005] Embodiments of this disclosure include catalyst systems. The catalyst systems include a metal–ligand complex according to formula (I):



[0006] In formula (I), M is a metal chosen from zirconium or hafnium, the metal having a formal oxidation state of +2, +3, or +4. Each X is a monodentate or bidentate ligand chosen from (C₁–C₄₀)hydrocarbyl, (C₆–C₂₀)aryl, or (C₆–C₂₀)heteroaryl. Subscript n of (X)_n is 2 or 3.

[0007] In formula (I), R¹, R², R^{5a}, R^{5b}, and R⁶ are independently chosen from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –N(R^N)₂, –OR^C, halogen, or hydrogen; optionally, R¹ and R² are covalently linked to form an aromatic ring. z₁ and z₂ are independently C(R^Z) or N, wherein each R^Z is –H or (C₁–C₃₀)hydrocarbyl; provided that at least one of z₁ and z₂ is N; and each R^C, R^N, and R^P in formula (I) is independently a (C₁–C₃₀)hydrocarbyl.

[0008] Embodiments of this disclosure include polymerization processes, particularly processes for producing ethylene-based polymers. The polymerization processes include contacting ethylene and optionally one or more (C₃–C₁₂)α-olefin in the presence of a catalyst system including a metal–ligand complex having a structure according to formula (I).

BRIEF DESCRIPTION OF FIGURES

[0009] FIG. 1 illustrates the Ligands 1 to 3.

[0010] FIG. 2A is a plot of the molecular weight of the polymer produced from the inventive and comparative procatalysts, in which $B(C_6F_5)_3$ is the cocatalyst and the polymerization reaction was run at 90 °C.

[0011] FIG. 2B is a plot of the molecular weight of the polymer produced from the inventive and comparative procatalysts, in which $B(C_6F_5)_3$ is the cocatalyst and the polymerization reaction was run at 120 °C.

[0012] FIG. 3A is a plot of the molecular weight of the polymer produced from the inventive and comparative procatalysts, in which bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane is the cocatalyst and the polymerization reaction was run at 90 °C.

[0013] FIG. 3B is a plot of the molecular weight of the polymer produced from the inventive and comparative procatalysts, in which bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane is the cocatalyst and the polymerization reaction was run at 120 °C.

DETAILED DESCRIPTION

[0014] 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.

[0015] Common abbreviations are listed below:

[0016] **R, Z, M, X and n**: as defined above; **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn**: benzyl; **i-Pr** : *iso*-propyl; **t-Bu** : *tert*-butyl; **t-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf** : trifluoromethane sulfonate; **THF** : tetrahydrofuran; **Et₂O** : diethyl ether; **CH₂Cl₂** : dichloromethane; **CV** : column volume (used in column chromatography); **EtOAc** : ethyl acetate;

C₆D₆ : deuterated benzene or benzene-*d*₆ ; **CDCl₃** : deuterated chloroform; **Na₂SO₄** : sodium sulfate; **MgSO₄** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi**: butyllithium; ***t*-BuLi** : *tert*-butyllithium; **Cu₂O** : Copper (I) Oxide; ***N,N'*-DMEDA**: *N,N'*-dimethylethylenediamine; **K₃PO₄**: Potassium phosphate tribasic; **Pd(AmPhos)Cl₂**: Bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II); **Pd(dppf)Cl₂**: [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride; **K₂CO₃**: potassium carbonate; **Cs₂CO₃**: cesium carbonate; ***i*-PrOBPin**: 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; **BrCl₂CCl₂Br**: 1,2-dibromotetrachloroethane; **HfCl₄** : hafnium(IV) chloride; **HfBn₄** : hafnium(IV) tetrabenzyl; **ZrCl₄** : zirconium(IV) chloride; **ZrBn₄** : zirconium(IV) tetrabenzyl; **ZrBn₂Cl₂(OEt₂)** : zirconium (IV) dibenzyl dichloride mono-diethyletherate; **HfBn₂Cl₂(OEt₂)** : hafnium (IV) dibenzyl dichloride mono-diethyletherate; **TiBn₄**: titanium (IV) tetrabenzyl; **N₂** : nitrogen gas; **PhMe**: toluene; **PPR** : parallel polymerization reactor; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **GC** : gas chromatography; **LC** : liquid chromatography; **NMR** : nuclear magnetic resonance; **MS**: mass spectrometry; **mmol** : millimoles; **mL** : milliliters; **M** : molar; **min or mins**: minutes; **h or hrs** : hours; **d**: days; **R_f**: retention fraction; **TLC** ; thin-layered chromatography; **rpm**: revolution per minute.

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

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

[0019] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₅₀)alkyl is an alkyl group having from 1 to 50 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S. An R^S substituted version of a chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–C₅₀)alkyl substituted with exactly one group R^S, where R^S is

phenyl ($-\text{C}_6\text{H}_5$)” may contain from 7 to 56 carbon atoms. Thus, in general when a chemical group defined using the “(C_x-C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^{S} , the minimum and maximum total number of carbon atoms of the chemical group is determined by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^{S} .

[0020] The term “substitution” means that at least one hydrogen atom ($-\text{H}$) 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 “ $-\text{H}$ ” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “ $-\text{H}$ ” are interchangeable, and unless clearly specified have identical meanings.

[0021] The term “(C_1-C_{50})hydrocarbonyl” means a hydrocarbon radical of from 1 to 50 carbon atoms, in which each hydrocarbon radical 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.

[0022] In this disclosure, a (C_1-C_{50})hydrocarbonyl may be an unsubstituted or substituted (C_1-C_{50})alkyl, (C_3-C_{50})cycloalkyl, (C_3-C_{20})cycloalkyl-(C_1-C_{20})alkylene, (C_6-C_{40})aryl, or (C_6-C_{20})aryl-(C_1-C_{20})alkylene (such as benzyl ($-\text{CH}_2-\text{C}_6\text{H}_5$)).

[0023] The terms “(C_1-C_{50})alkyl” and “(C_1-C_{18})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 (C_1-C_{50})alkyl are unsubstituted (C_1-C_{20})alkyl; unsubstituted (C_1-C_{10})alkyl; unsubstituted (C_1-C_5)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 (C_1-C_{40})alkyl are substituted (C_1-C_{20})alkyl, substituted (C_1-C_{10})alkyl, trifluoromethyl, and [C_{45}]alkyl. The term “[C_{45}]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.

[0024] 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. When the bicyclic or tricyclic aromatic hydrocarbon radical is present, at least one of the rings of the radical is aromatic. The other ring or rings of the aromatic radical may be independently fused or non-fused and aromatic or non-aromatic. 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.

[0025] 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. Examples of unsubstituted (C₃–C₄₀)cycloalkyl are unsubstituted (C₃–C₂₀)cycloalkyl, unsubstituted (C₃–C₁₀)cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C₃–C₄₀)cycloalkyl are substituted (C₃–C₂₀)cycloalkyl, substituted (C₃–C₁₀)cycloalkyl, cyclopentanone-2-yl, and 1-fluorocyclohexyl.

[0026] 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.

[0027] 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.

[0028] 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, or 3; and each heteroatom may be O, S, N, or P. Examples of 5-membered ring heteroaromatic hydrocarbon radicals include pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; and tetrazol-5-yl. The 6-membered ring has 6 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1 or 2 and the heteroatoms may be N or P. Examples of 6-membered ring heteroaromatic hydrocarbon radicals include pyridine-2-yl; pyrimidin-2-yl; and pyrazin-2-yl. The bicyclic heteroaromatic hydrocarbon radical can be a fused 5,6- or 6,6-ring system. Examples of the fused 5,6-ring system bicyclic heteroaromatic hydrocarbon radical are indol-1-yl; and benzimidazole-1-yl. Examples of the fused 6,6-ring system bicyclic heteroaromatic hydrocarbon radical are quinolin-2-yl; and isoquinolin-1-yl. The tricyclic heteroaromatic hydrocarbon radical can be a fused 5,6,5-; 5,6,6-; 6,5,6-; or 6,6,6-ring system. An example of the fused 5,6,5-ring system is 1,7-dihydropyrrolo[3,2-f]indol-1-yl. An example of the fused 5,6,6-ring system is 1H-benzo[f]indol-1-yl. An example of the fused 6,5,6-ring system is 9H-carbazol-9-yl. An example of the fused 6,5,6- ring system is 9H-carbazol-9-yl. An example of the fused 6,6,6-ring system is acrydin-9-yl.

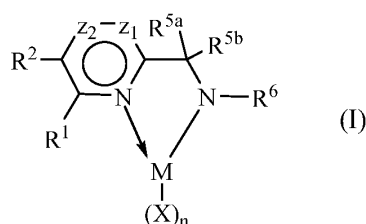
[0029] The term “(C₁–C₅₀)heteroalkyl” means a saturated straight or branched chain radicals containing one to fifty carbon atoms, or fewer carbon atoms and one or more of the heteroatoms. The term “(C₁–C₅₀)heteroalkylene” means a saturated straight or branched chain diradicals containing from 1 to 50 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 .

[0030] Examples of unsubstituted (C₂–C₄₀)heterocycloalkyl include unsubstituted (C₂–C₂₀)heterocycloalkyl, unsubstituted (C₂–C₁₀)heterocycloalkyl, aziridin-1-yl, oxetan-2-yl, tetrahydrofuran-3-yl, pyrrolidin-1-yl, tetrahydrothiophen-S,S-dioxide-2-yl, morpholin-4-yl, 1,4-dioxan-2-yl, hexahydroazepin-4-yl, 3-oxa-cyclooctyl, 5-thio-cyclononyl, and 2-aza-cyclodecyl.

[0031] 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⁻).

[0032] 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.

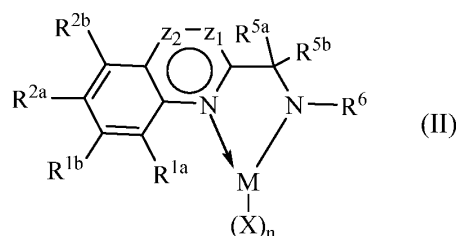
[0033] Embodiments of this disclosure include procatalysts, catalyst systems, and polymerization processes that include the catalyst systems of this disclosure. The catalyst systems include a metal–ligand complex according to formula (I):



[0034] In formula (I), M is a metal chosen from zirconium or hafnium, the metal having a formal oxidation state of +2, +3, or +4. Each X is a monodentate or bidentate ligand chosen from (C₁–C₄₀)hydrocarbyl, (C₆–C₂₀)aryl, or (C₆–C₂₀)heteroaryl. Subscript n of (X)_n is 2 or 3.

[0035] In formula (I), R¹, R², R^{5a}, R^{5b}, and R⁶ are independently chosen from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –N(R^N)₂, –OR^C, halogen, or hydrogen; optionally, R¹ and R² are covalently linked to form an aromatic ring. z₁ and z₂ are independently C(R^Z) or N, wherein each R^Z is –H or (C₁–C₃₀)hydrocarbyl; provided that at least one of z₁ and z₂ is N; and each R^C, R^N, and R^P in formula (I) is independently a (C₁–C₃₀)hydrocarbyl.

[0036] In one or more embodiments, R^1 and R^2 are covalently linked to form an aromatic ring, and the metal–ligand complex according to formula (II):



[0037] In formula (II), R^{1a} , R^{1b} , R^{2a} , R^{2b} are independently (C_1-C_{30}) alkyl or $-H$; and R^{5a} , R^{5b} , z_1 , z_2 , X , n , and M are as defined in formula (I).

[0038] In one or more embodiments, in formula (I), z_1 is $C(R^Z)$ and z_2 is N , wherein in R^Z is $-H$ or (C_1-C_{30}) hydrocarbyl. In other embodiments, z_1 is N and z_2 is $C(R^Z)$, wherein in R^Z is $-H$ or (C_1-C_{30}) hydrocarbyl.

[0039] In one or more embodiments, R^Z is hydrogen or (C_1-C_{20}) alkyl. In various embodiments, R^Z is hydrogen, methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-methylpropyl, 1,1-dimethylethyl, *n*-pentyl, cyclopentyl, *n*-hexyl, heptyl, *n*-octyl, or *tert*-octyl.

[0040] In various embodiments, in formulas (I) or (II), R^6 is a substituted (C_6-C_{40}) aryl or an unsubstituted (C_6-C_{40}) aryl. In one or more embodiments, R^6 is independently selected from phenyl, benzyl, (2,4,6-tri-*iso*-propyl)phenyl, (2,6-di-*iso*-propyl)phenyl, 3,5-di-*tert*-butylphenyl, naphthyl, or cyclopropyl.

[0041] In some embodiments, in formulas (I) or (II), R^6 is hydrogen, R^{5a} is hydrogen, and R^{5b} is independently chosen from (C_1-C_{40}) hydrocarbyl or (C_1-C_{40}) heterohydrocarbyl. In one or more embodiments, R^{5b} is independently chosen from phenyl, benzyl, (2,4,6-tri-*iso*-propyl)phenyl, (2,6-di-*iso*-propyl)phenyl, 3,5-di-*tert*-butylphenyl, naphthyl, or cyclopropyl. In some embodiments, at least one of R^{5a} and R^{5b} is (C_1-C_{40}) hydrocarbyl or (C_1-C_{40}) heterohydrocarbyl.

[0042] In one or more embodiments, only one of R^{5a} and R^{5b} is selected from the group consisting of pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; tetrazol-5-yl; pyridine-2-yl; pyrimidin-2-yl; pyrazin-2-yl; quinolin-2-yl; isoquinolin-1-yl; and 9H-carbazol-9-yl.

[0043] In one or more embodiments, in formula (II), R^{1a} , R^{1b} , R^{2a} , R^{2b} are independently hydrogen, methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-methylpropyl, 1,1-dimethylethyl, *n*-pentyl, cyclopentyl, *n*-hexyl, heptyl, *n*-octyl, or *tert*-octyl.

[0044] In the metal–ligand complex according to formula (I) or formula (II), each X bonds with M through a covalent bond, a dative bond, or an ionic bond. In some embodiments, each X is identical. The metal–ligand complex has 6 or fewer metal–ligand bonds and can be overall charge-neutral or may have a positive-charge associated with the metal center. In some embodiments, the catalyst system includes a metal–ligand complex according to formula (I), in which M is zirconium or hafnium; each X is independently chosen from (C_1-C_{20}) alkyl, (C_1-C_{20}) heteroalkyl, (C_6-C_{20}) aryl, (C_4-C_{20}) heteroaryl, (C_4-C_{12}) diene, or a halogen. In one or more embodiments, each X is independently benzyl, phenyl, or chloro.

[0045] In some embodiments, the monodentate ligand may be a monoanionic ligand. Monoanionic ligands have a net formal oxidation state of -1 . Each monoanionic ligand may independently be hydride, (C_1-C_{40}) hydrocarbyl carbanion, (C_1-C_{40}) heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, sulfate, $HC(O)O^-$, $HC(O)N(H)^-$, (C_1-C_{40}) hydrocarbylC(O) O^- , (C_1-C_{40}) hydrocarbylC(O)N $((C_1-C_{20})$ hydrocarbyl) $^-$, (C_1-C_{40}) 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}) hydrocarbyl, or (C_1-C_{40}) heterohydrocarbyl, or R^K and R^L are taken together to form a (C_2-C_{40}) hydrocarbylene or (C_1-C_{20}) heterohydrocarbylene and R^M is as defined above.

[0046] In other embodiments, at least one monodentate ligand X, independently from any other ligands X, may be a neutral ligand. In specific embodiments, the neutral ligand is a neutral Lewis base group such as $R^Q N R^K R^L$, $R^K O R^L$, $R^K S R^L$, or $R^Q P R^K R^L$, where each R^Q independently is hydrogen, $[(C_1-C_{10})$ hydrocarbyl] $_3 Si (C_1-C_{10})$ hydrocarbyl, (C_1-C_{40}) hydrocarbyl, $[(C_1-C_{10})$ hydrocarbyl] $_3 Si$, or (C_1-C_{40}) heterohydrocarbyl and each R^K and R^L independently is as previously defined.

[0047] Additionally, each X can be a monodentate ligand that, independently from any other ligands X, is a halogen, unsubstituted (C_1-C_{20}) hydrocarbyl, unsubstituted (C_1-C_{20}) hydrocarbylC(O) O^- , or $R^K R^L N^-$, wherein each of R^K and R^L independently is an

unsubstituted(C₁–C₂₀)hydrocarbyl. In some embodiments, each monodentate ligand X is a chlorine atom, (C₁–C₁₀)hydrocarbyl (e.g., (C₁–C₆)alkyl or benzyl), unsubstituted (C₁–C₁₀)hydrocarbylC(O)O–, or R^KR^LN–, wherein each of R^K and R^L independently is an unsubstituted (C₁–C₁₀)hydrocarbyl. In one or more embodiments of formula (I), (II), and (III), X is benzyl, chloro, –CH₂SiMe₃, or phenyl.

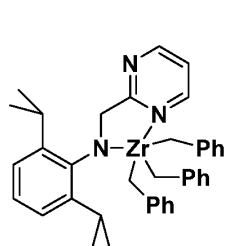
[0048] In further embodiments, each X is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 1,1-dimethylethyl; 2-methylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments, each X is the same. In other embodiments, at least two X are different from each other. In the embodiments in which at least two X are different from at least one X, X is a different one of methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 1,1-dimethylethyl; 2-methylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In further embodiments, the bidentate ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0049] 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.

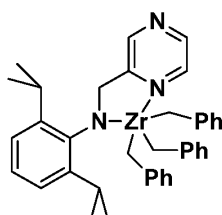
[0050] Embodiments of this disclosure include polymerization processes. The polymerization processes include contacting ethylene and optionally one or more (C₃–C₁₂) α -olefin in the presence of a catalyst system under olefin polymerization conditions to form an ethylene-based polymer. The catalyst system includes a metal–ligand complex according to formula (I).

[0051] Embodiments of this disclosure include procatalysts. The procatalysts may be suitable for use as metal–ligand complexes in polymerization processes. Procatalysts according to embodiments are metal–ligand complexes having formula (I) or formula (II) as previously described with respect to the catalyst systems.

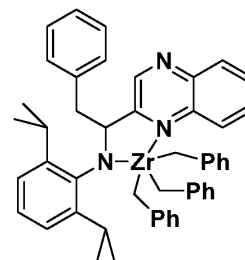
[0052] In illustrative embodiments, the catalyst systems may include a metal–ligand complex according to formula (I) having the structure of any of the Procatalysts 1–22 listed below. The Procatalysts 1–6 may be synthesized from the corresponding Ligands 1–3, as shown in FIG. 1:



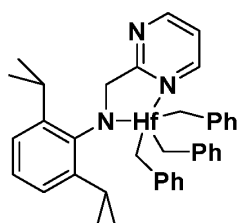
Procatalyst 1



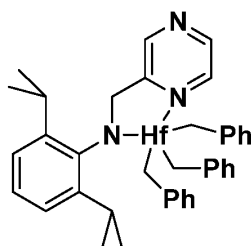
Procatalyst 2



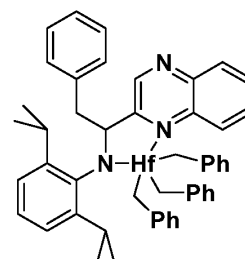
Procatalyst 3



Procatalyst 4



Procatalyst 5



Procatalyst 6

Cocatalyst Component

[0053] The catalyst system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, the procatalyst according to a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Additionally, the metal–ligand complex according for formula (I) includes both a procatalyst form, which is neutral, and a catalytic form, which may be positively charged due to the loss of a monoanionic ligand, such 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.

[0054] 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.

[0055] 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.

[0056] 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 aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) amine, and combinations thereof.

[0057] 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 aluminoxane 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 aluminoxane alone is used as the activating co-catalyst, preferably the number of moles of the aluminoxane 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).

Polyolefins

[0058] 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.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] 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.

[0063] 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.

[0064] 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.

[0065] 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.

[0066] 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 0.950 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.

[0067] 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 15, 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.

[0068] 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.

[0069] 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.

[0070] 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 VNMRS-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.

General Procedure for PPR Screening Experiments

[0071] Polyolefin catalysis screening is performed in a high throughput parallel pressure reactor (PPR) system. The PPR system is composed of an array of 48 single-cell (6 x 8 matrix) reactors in an inert-atmosphere glovebox. Each cell is equipped with a glass insert with an internal working liquid volume of approximately 5 mL. Each cell has independent controls for pressure, and the liquid in the cell is continuously stirred at 800 rpm. Catalyst solutions, unless otherwise noted, are prepared by dissolving an appropriate amount of a procatalyst in toluene. All liquids (for example, solvent, 1-octene, chain shuttling agent solutions as appropriate to the experiment, and catalyst solutions) are added to the single-cell reactors via robotic syringes. Gaseous reagents (i.e. ethylene, H_2) are added to the single-cell reactors via a gas injection port. Prior to each run, the reactors are heated to 80 $^\circ\text{C}$, purged with ethylene, and vented.

[0072] A portion of Isopar-E is added to the reactors. The reactors are heated to the run temperature and pressured to the appropriate psig with ethylene. Toluene solutions of reagents are added in the following order: (1) 1-octene with 500 nmol of scavenger MMAO-3A; (2) activator (cocatalyst-1, cocatalyst-2, etc); and (3) catalyst.

[0073] Each liquid addition is chased with a small amount of Isopar-E so that after the final addition, a total reaction volume of 5 mL is reached. Upon addition of the catalyst, the PPR software begins monitoring the pressure of each cell. The pressure (within approximately 2-6 psig) is maintained by the supplemental addition of ethylene gas by opening the valve at the set point

minus 1 psi and closing it when the pressure reached 2 psi higher. All drops in pressure are cumulatively recorded as “Uptake” or “Conversion” of the ethylene for the duration of the run or until the uptake or conversion requested value is reached, whichever occurs first. Each reaction is quenched with the addition of 10% carbon monoxide in argon for 4 minutes at 40-50 psi higher than the reactor pressure. A shorter “Quench Time” means that the catalyst is more active. In order to prevent the formation of too much polymer in any given cell, the reaction is quenched upon reaching a predetermined uptake level (50 psig for 120 °C runs, 75 psig for 150 °C runs). After all the reactions are quenched, the reactors are allowed to cool to 70 °C. The reactors are vented, purged for 5 minutes with nitrogen to remove carbon monoxide, and the tubes are removed. The polymer samples are dried in a centrifugal evaporator at 70 °C for 12 hours, weighed to determine polymer yield, and submitted for IR (1-octene incorporation) and GPC (molecular weight) analysis.

SymRAD HT-GPC Analysis

[0074] The molecular weight data is determined by analysis on a hybrid Symyx/Dow built Robot-Assisted Dilution High-Temperature Gel Permeation Chromatographer (Sym-RAD-GPC). The polymer samples are dissolved by heating for 120 minutes at 160°C in 1,2,4-trichlorobenzene (TCB) at a concentration of 10 mg/mL stabilized by 300 parts per million (ppm) of butylated hydroxyl toluene (BHT). Each sample was diluted to 1 mg/mL immediately before the injection of a 250 µL aliquot of the sample. The GPC is equipped with two Polymer Labs PLgel 10 µm MIXED-B columns (300 x 10 mm) at a flow rate of 2.0 mL/minute at 160°C. Sample detection is performed using a PolyChar IR4 detector in concentration mode. A conventional calibration of narrow polystyrene (PS) standards is utilized with apparent units adjusted to homo-polyethylene (PE) using known Mark-Houwink coefficients for PS and PE in TCB at this temperature.

1-Octene Incorporation IR Analysis

[0075] The running of samples for the HT-GPC analysis precedes the IR analysis. For the IR analysis, a 48-well HT silicon wafer is utilized for deposition and analysis of 1-octene incorporation of samples. For the analysis, the samples are heated to 160 °C for less than or equal to 210 minutes; the samples are reheated to remove magnetic GPC stir bars and are shaken with glass-rod stir bars on a J-KEM Scientific heated robotic shaker. Samples are deposited while being heated using a Tecan MiniPrep 75 deposition station, and the 1,2,4-trichlorobenzene is

evaporated off the deposited wells of the wafer at 160°C under nitrogen purge. The analysis of 1-octene is performed on the HT silicon wafer using a NEXUS 670 E.S.P. FT-IR.

Batch Reactor Polymerization Procedure

[0076] The batch reactor polymerization reactions are conducted in a 4 L Parr™ batch reactor. The reactor is heated by an electrical heating mantle, and is cooled by an internal serpentine cooling coil containing cooling water. Both the reactor and the heating/cooling system are controlled and monitored by a Camile™ TG process computer. The bottom of the reactor is fitted with a dump valve that empties the reactor contents into a stainless steel dump pot. The dump pot is prefilled with a catalyst kill solution (typically 5 mL of an Irgafos / Irganox / toluene mixture). The dump pot is vented to a 30 gallon blow-down tank, with both the pot and the tank purged with nitrogen. All solvents used for polymerization or catalyst makeup are run through solvent purification columns to remove any impurities that may affect polymerization. The 1-octene and IsoparE are passed through two columns, the first containing A2 alumina, the second containing Q5. The ethylene is passed through two columns, the first containing A204 alumina and 4Å molecular sieves, the second containing Q5 reactant. The N₂, used for transfers, is passed through a single column containing A204 alumina, 4Å molecular sieves and Q5.

[0077] The reactor is loaded first from the shot tank that may contain IsoparE solvent and/or 1-octene, depending on reactor load. The shot tank is filled to the load set points by use of a lab scale to which the shot tank is mounted. After liquid feed addition, the reactor is heated up to the polymerization temperature set point. If ethylene is used, it is added to the reactor when the ethylene is at the reaction temperature to maintain reaction pressure set point. The amount of ethylene added is monitored by a micro-motion flow meter. For some experiments, the standard conditions at 120 °C are 88 g ethylene and 568 g 1-octene in 1155 g of IsoparE, and the standard conditions at 150 °C are 81 g ethylene and 570 g 1-octene in 1043 g of IsoparE.

[0078] The procatalyst and activators are mixed with the appropriate amount of purified toluene to achieve a molarity solution. The procatalyst and activators are handled in an inert glove box, drawn into a syringe and pressure transferred into the catalyst shot tank. The syringe is rinsed three times with 5 mL of toluene. Immediately after the catalyst is added, the run timer begins. If ethylene is used, it is added by the Camile to maintain reaction pressure set point in the reactor. The polymerization reactions are run for 10 minutes, then the agitator is stopped, and the bottom

dump valve is opened to empty reactor contents to the dump pot. The contents of the dump pot are poured into trays and placed in a lab hood where the solvent was evaporated off overnight. The trays containing the remaining polymer are transferred to a vacuum oven, where they are heated up to 140°C under vacuum to remove any remaining solvent. After the trays cool to ambient temperature, the polymers were weighed for yield to measure efficiencies, and submitted for polymer testing.

EXAMPLES

[0079] Examples 1 to 6 are synthetic procedures for ligand intermediates, ligands, and isolated procatalysts. Structures of Ligands 1 to 3 are provided in FIG. 1. Procatalysts 1 to 6 were synthesized from the Ligands 1 to 3. Example 7 provides the reaction conditions and polymerization procedure. In Example 8, the results of the polymerization reactions of Procatalysts 1 – 6 are tabulated and discussed. One or more features of the present disclosure are illustrated in view of the examples as follows:

[0080] Example 1 – Synthesis of Intermediate 1. Diazinylimines 1 was prepared by condensation of the corresponding aldehyde with 2,6-diisopropyl aniline in methanol. Aldehyde (1.0 g, 9.2 mmol) dissolved in methanol (20 mL) was stirred at room temperature while neat aniline (1.8 g, 10.2 mmol) was added dropwise. The mixture was blanketed under inert atmosphere and heated at 65 °C for 24 hours. Intermediate 1 was precipitated from 2:1 toluene/hexanes at -10 °C in 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.96 (d, J = 4.9 Hz, 1H), 8.35 (s, 1H), 7.40 (t, J = 4.9 Hz, 1H), 7.20 – 7.11 (m, 2H), 3.00 (hept, J = 6.9 Hz, 1H), 1.69 (s, 1H), 1.17 (d, J = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 161.97, 161.66, 157.97, 148.46, 137.29, 124.91, 123.18, 121.68, 28.02, 23.81.

[0081] Example 2 – Synthesis of Intermediate 2. Diazinylimine 2 was prepared by condensation of the corresponding aldehyde with 2,6-diisopropyl aniline in methanol. Aldehyde (1.0 g, 9.2 mmol) dissolved in methanol (20 mL) was stirred at room temperature while neat aniline (1.8 g, 10.2 mmol) was added dropwise. The mixture was blanketed under inert atmosphere and heated at 65 °C for 24 hours. Intermediate 2 was precipitated at -10 °C from 2:1 toluene/hexanes in 28% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.49 (dd, J = 1.5, 0.5 Hz, 1H), 8.72 – 8.64 (m, 2H), 8.34 (d, J = 0.5 Hz, 1H), 7.22 – 7.11 (m, 3H), 2.96 (hept, J = 6.8 Hz, 2H), 1.64 (s,

1H), 1.19 (d, J = 6.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 161.32, 149.37, 148.15, 145.98, 144.36, 143.77, 137.28, 125.06, 123.32, 28.18, 23.60.

[0082] Example 3 – Synthesis of Intermediate 3. Neat 2,6-diisopropyl aniline (1.51 g, 8.52 mmol) was added dropwise to a stirred red suspension of quinoxaline-2-carboxaldehyde (0.934 g, 5.91 mmol) in dichloromethane (15 mL) at room temperature, followed by solid magnesium sulfate (1 g) added in a single portion. The red-orange suspension was stirred overnight under inert atmosphere. The mixture was filtered after 24 hours at room temperature. The combined red solution was diluted with two volume equivalents of methanol and a few drops of hexanes, then cooled at -10 °C. The product was recovered as orange needles in 39% yield (1.060 g, 3.34 mmol). ¹H NMR (400 MHz, CDCl₃) δ 9.80 (s, 1H), 8.50 (d, J = 0.4 Hz, 1H), 8.24 – 8.15 (m, 2H), 7.91 – 7.79 (m, 2H), 7.24 – 7.13 (m, 3H), 3.01 (hept, J = 6.9 Hz, 2H), 1.21 (d, J = 6.8 Hz, 13H). ¹³C NMR (101 MHz, CDCl₃) δ 161.97, 148.49, 148.21, 143.84, 143.42, 142.12, 137.22, 131.30, 130.70, 129.96, 129.66, 125.13, 123.33, 28.23, 23.61.

[0083] Example 4 – Synthesis of Ligand 1. A 200 mL sidearm flask with a stir bar was charged with Intermediate 1 (0.5 g, 2 mmol) under inert atmosphere. With N₂ outflow, methanol (50 mL) was added. The flask was cooled in an ice bath for 15 minutes and solid NaBH₄ (0.75 g, 20 mmol) was added portionwise under gentle N₂ purge. Gas evolution was observed during addition. After complete addition, the flask remained in the ice bath as the yellow mixture was allowed to stir under inert atmosphere and slowly warm to room temperature overnight. The reaction was quenched by addition of an aqueous ammonium chloride solution (75 mL), and the resulting suspension was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic phases were dried over Na₂SO₄ and evacuated to dryness on the rotavap. Pyrimidine amine Ligand 1 was isolated as a yellow-orange oil in 88% yield. ¹H NMR (400 MHz, C₆D₆) δ 8.14 (d, J = 4.9 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.19 – 6.11 (m, 3H), 4.84 (s, 1H), 4.58 (s, 1H), 3.67 (hept, J = 6.8 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.10, 157.22, 143.35, 142.61, 123.94, 123.75, 119.47, 57.02, 27.99, 24.41.

[0084] Example 5 – Synthesis of Ligand 2. A 200 mL sidearm flask with a stir bar was charged with Intermediate 2 (0.5 g, 2 mmol) under inert atmosphere. With N₂ outflow, methanol (50 mL) was added. The flask was cooled in an ice bath for 15 minutes and solid NaBH₄ (0.75 g,

20 mmol) was added portionwise under gentle N₂ purge. Gas evolution was observed during addition. After complete addition, the flask remained in the ice bath as the yellow mixture was allowed to stir under inert atmosphere and slowly warm to room temperature overnight. The reaction was quenched by addition of an aqueous ammonium chloride solution (75 mL), and the resulting suspension was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic phases were dried over Na₂SO₄ and evacuated to dryness on the rotavap. Pyrazine amine Ligand 2 was isolated as a yellow-orange oil in 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.49 (dd, J = 1.5, 0.5 Hz, 1H), 8.72 – 8.64 (m, 2H), 8.34 (d, J = 0.5 Hz, 1H), 7.22 – 7.11 (m, 3H), 2.96 (hept, J = 6.8 Hz, 2H), 1.64 (s, 1H), 1.19 (d, J = 6.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.72, 144.19, 144.18, 143.51, 142.97, 142.53, 124.52, 123.85, 54.57, 27.92, 24.39.

[0085] Example 6 – In Situ Synthesis of Procatalysts 1 – 6. Small scale reactions were conducted by separately preparing 5 or 10 mM stock solutions of M(CH₂Ph)₄ and Ligand 1, 2, or 3 in C₆D₆ or toluene in the glovebox. The solutions were combined in the desired stoichiometry and mixed thoroughly at ambient temperature. When monitored by ¹H NMR spectroscopy after at least 30 minutes showed complete conversion to the desired procatalyst under conditions relevant to Parallel Pressure Reactor (PPR) polymerization experiments.

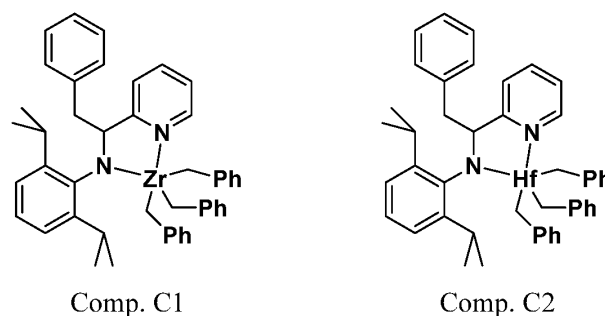
[0086] Example 7 – PPR Polymerization Experiments. Octene loading was determined for an initial octene:ethylene molar ratio of 2.24 at the selected temperature and pressure (90°C/100.5 psig, 120°C/150.0 psig, or 150°C/213.4 psig) providing ethylene-starved conditions for each experiment. Copolymerization screens were performed by hand-mixing a toluene solution of ZrBn₄ or HfBn₄ with a toluene solution of Ligand 1, 2, or 3 and allowed to react for at least 1 hour at ambient glovebox temperature. Each solution was separately activated with either B(C₆F₅)₃ (5 equiv.) or [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄] (1.5 equiv.), and each reactor vessel was charged with isopar-E to reach a total volume of 5.0 mL and MMAO-3A (500 nmol) producing at least 20 mg polymer. Molecular weight distribution (M_w, M_n) was determined by analysis on a Robotic Assisted Dilution High Temperature Gel Permeation Chromatographer (SymRAD-GPC). Polymer samples were dissolved in 1,2,4-trichlorobenzene (TCB; stabilized by 300 ppm BHT) at 170 °C. Samples were diluted to a 1 mg/mL sample concentration and dispensed in 400 µL aliquots for each injection, with a 10 minute stagger between injections. The GPC utilized two (2) Polymer Labs PLgel 10µm MIXED-B columns (300x10mm) at a flow rate of 2.0mL/minute

at 160°C. Sample detection was performed using a PolyChar IR4 detector in concentration mode. A conventional calibration of narrow polystyrene (PS) standards was utilized, with apparent units adjusted to polyethylene (PE) using known Mark-Houwink coefficients for PS and PE in TCB at 160°C. Decane was used as a flow marker to ensure flow-rate integrity for both the calibration set and the experimental samples. Data was depicted using PolyChar GPC software.

[0087] Example 8 – Polymerization Reactions

[0088] Catalyst activity (in terms of quench time and polymer yield) and resulting polymer characteristics were assessed for Procatalysts 1–6. The polymerization reactions were carried out in a batch reactor and parallel pressure reactor (PPR).

[0089] Procatalysts 1–6 were compared to comparative procatalysts, Comparative C1 (Comp. C1) and Comparative C2 (Comp C2). The structures of Comp. C1 and Comp C2 are shown below:



[0090] The results recorded in Tables 1 to 4 were produced from procatalysts generated *in situ*. The polymerization experiments were conducted in a PPR reactor at 90 °C, 120 °C or 150 °C using an activator and MMAO-3 (500 nmoles at 120 °C or 750 nmoles at 150 °C) was employed as the scavenger. In Table 1, [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄] was the activator in amounts of 1.5 molar equivalents in relation to the procatalyst. In Table 2, B(C₆F₅)₃ was the activator in amounts of 5 molar equivalents in relation to the procatalyst, and.

Table 1: Polymerization Results with [HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄] as the Activator

Procatalyst	Ligand umol	Mol% C ₈	M _n	M _w (g/mol)	PDI	C ₂ Uptake (psig)	Pressure (psig)	Temp (°C)	Yield (g)	Time (s)
Comp 1	0.1	9.8	23,194	372,407	16.1	51	100.5	90	0.144	54
	0.1	9.7	15,685	363,592	23.2	51	100.5	90	0.149	51
	0.1	7.8	21,966	210,813	9.6	50	150	120	0.110	64
	0.1	8.2	20,285	212,171	10.5	51	150	120	0.109	53

	0.1	7.7	19,926	212,633	10.7	50	150	120	0.114	53
	0.2	5.9	9,570	102,894	10.8	75	213.4	150	0.104	390
	0.2	5.4	7,598	108,168	14.2	75	213.4	150	0.105	630
Comp 2	0.1	22.9	13,070	164,664	12.6	51	100.5	90	0.299	47
	0.1	19.2	15,027	197,420	13.1	52	100.5	90	0.297	50
	0.1	15.4	17,962	109,499	6.1	52	150	120	0.240	30
	0.1	16.6	14,949	107,521	7.2	52	150	120	0.235	21
	0.1	17.3	13,465	104,391	7.8	54	150	120	0.238	27
	0.1	5.3	55,909	210,247	3.8	36	213.4	150	0.049	1800
	0.1	5.2	48,531	205,837	4.2	27	213.4	150	0.032	1801
	0.2	11.6	11,316	57,883	5.1	76	213.4	150	0.190	35
	0.2	9.2	10,052	60,039	6.0	78	213.4	150	0.200	39
Procat. 1	0.1	4.2	27,220	495,470	18.2	51	150	120	0.083	209
	0.1	4.3	23,343	460,633	19.7	50	150	120	0.077	175
	0.1	4.1	19,697	378,664	19.2	50	150	120	0.079	218
	0.1	4.1	18,804	380,053	20.2	50	150	120	0.079	218
	0.2	3.6	4,070	123,670	30.4	68	213.4	150	0.070	1800
Procat. 2	0.1	4.8	30,161	608,228	20.2	50	150	120	0.049	970
	0.1	4.7	25,430	656,569	25.8	50	150	120	0.052	1581
	0.1	4.5	33,361	586,802	17.6	50	150	120	0.068	486
	0.1	5.1	20,136	587,213	29.2	50	150	120	0.068	316
	0.2	3.7	8,482	195,207	23.0	16	213.4	150	0.021	1801
Procat. 3	0.1	11.7	105,357	653,363	6.2	50	100.5	90	0.133	159
	0.1	9.2	101,559	642,994	6.3	51	100.5	90	0.123	68
	0.1	5.6	43,259	487,305	11.3	50	150	120	0.071	153
	0.1	5.8	40,005	504,886	12.6	50	150	120	0.075	253
	0.1	7.0	70,902	459,616	6.5	50	150	120	0.071	152
	0.1	8.1	62,758	426,011	6.8	50	150	120	0.071	265
	0.1	7.5	37,618	400,984	10.7	50	150	120	0.077	430
	0.2	4.5	12,774	262,146	20.5	44	213.4	150	0.056	1801
	0.2	4.6	9,693	270,617	27.9	45	213.4	150	0.059	1801
Procat. 4	0.1	4.5	55,683	427,797	7.7	50	150	120	0.095	293
	0.1	4.7	29,620	433,366	14.6	50	150	120	0.089	378
	0.2	5.2	18,431	103,334	5.6	75	213.4	150	0.143	98
	0.2	6.0	11,908	101,512	8.5	76	213.4	150	0.165	57
Procat. 5	0.1	5.0	35,378	649,600	18.4	26	150	120	0.030	1801
	0.1	4.8	30,526	623,708	20.4	28	150	120	0.028	1801
	0.2	4.2	29,244	332,296	11.4	57	213.4	150	0.076	1801
	0.2	3.9	20,832	346,178	16.6	44	213.4	150	0.058	1801
Procat. 6	0.1	12.6	177,878	755,524	4.3	51	100.5	90	0.215	64
	0.1	12.6	152,008	695,121	4.6	53	100.5	90	0.169	68
	0.1	11.6	85,776	355,964	4.2	51	150	120	0.152	66
	0.1	11.1	65,411	336,820	5.2	51	150	120	0.139	70
	0.2	7.0	36,817	162,368	4.4	69	213.4	150	0.101	1800
	0.2	6.9	26,925	153,436	5.7	70	213.4	150	0.101	1800

Table 2: Polymerization Results with B(C₆F₅)₃ as the Activator

Procatalyst	Ligand μmol	Mol% C ₈	M _n	M _w (g/mol)	PDI	C ₂ Uptake (psig)	Pressure (psig)	Temp (°C)	Yield (g)	Time (s)
Comp 1	0.1	6.4	116,319	316,138	2.7	50	100.5	90	0.076	193
	0.1	5.6	102,716	293,688	2.9	50	100.5	90	0.071	250
	0.1	5.0	55,609	150,447	2.7	20	150	120	0.02	1801
	0.1	5.1	56,139	157,497	2.8	23	150	120	0.021	1800
Comp 2	0.1	9.0	139,164	323,635	2.3	50	100.5	90	0.103	148
	0.1	9.4	138,450	326,326	2.4	51	100.5	90	0.105	131
	0.1	6.8	78,239	182,123	2.3	38	150	120	0.04	1801
	0.1	7.1	68,879	181,406	2.6	44	150	120	0.047	1802
	0.1	6.2	67,667	187,865	2.8	39	150	120	0.044	1801
Procat. 1	0.1	2.5	11,191	197,923	17.7	19	150	120	0.021	1800
	0.1	2.6	11,803	214,436	18.2	21	150	120	0.021	1802
	0.1	2.6	11,434	216,066	18.9	21	150	120	0.022	1802
	0.1	2.5	10,148	207,078	20.4	20	150	120	0.021	1801
	0.1	3.1	11,379	253,986	22.3	20	150	120	0.021	1800
Procat. 2	0.1	3.0	38,095	476,008	12.5	20	150	120	0.021	1802
	0.1	3.5	33,430	480,714	14.4	20	150	120	0.021	1801
Procat. 3	0.1	2.9	95,259	584,252	6.1	50	100.5	90	0.069	106
	0.1	2.5	85,288	571,595	6.7	51	100.5	90	0.069	95
	0.1	2.9	29,815	311,859	10.5	20	150	120	0.021	1801
Procat. 4	0.1	3.3	12,372	68,939	5.6	28	150	120	0.03	1802
	0.1	3.6	13,887	94,925	6.8	28	150	120	0.029	1801
	0.1	3.3	12,175	86,128	7.1	30	150	120	0.034	1800
	0.1	3.7	13,541	102,043	7.5	27	150	120	0.028	1801
	0.1	3.4	11,176	86,729	7.8	24	150	120	0.026	1802
	0.1	3.4	11,735	100,364	8.6	26	150	120	0.03	1800
Procat. 6	0.1	4.6	169,895	1,412,128	8.3	50	100.5	90	0.083	249
	0.1	4.9	132,093	1,378,669	10.4	50	100.5	90	0.081	589

[0091] Procatalysts 1 to 6 are analogs of diazine donors – pyrimidine, pyrazine, and quinoxaline. Procatalyst 1 to 6 produced high molecular weight polymers with incorporation of 1-octene ranging from 2 mole percent to 12 mole percent in PPR copolymerization screens.

[0092] Procatalyst 1 to 6 produced polymers having a molecular weight (M_w) greater than 400 kg/mol at 120 °C, and a molecular weight of greater than 250 kg/mol at 150 °C.

[0093] In Table 2, a quinoxaline derivative, Procatalyst 6 (Procat. 6) produced polymers exhibiting a molecular weight of greater 1,300 kg/mol at 90 °C.

[0094] The data recorded in the plots of FIG. 2A, FIG. 2B, FIG. 3A, and FIG. 3B indicate that the molecular weights of the polymers produced by the diazine donors, Procatalysts 1 to 6, are greater than those obtained for pyridine donors operating under identical PPR screening conditions.