

MULTIMODAL POLYMERIZATION PROCESSES WITH MULTI-CATALYST SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit of U.S. Provisional Application Serial No. 63/594,827 filed October 31, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[002] Embodiments of the present disclosure generally relate to olefin polymerization catalyst systems and processes, and, more specifically, to the olefin polymerization catalyst systems including one or more constrained geometry procatalysts and one or more guanidine procatalysts and polymerization processes incorporating the catalyst systems to produce bimodal polymers.

BACKGROUND

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

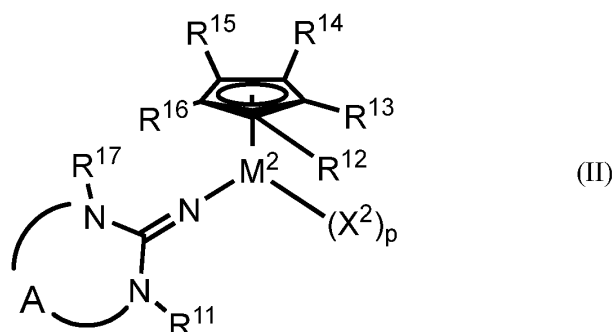
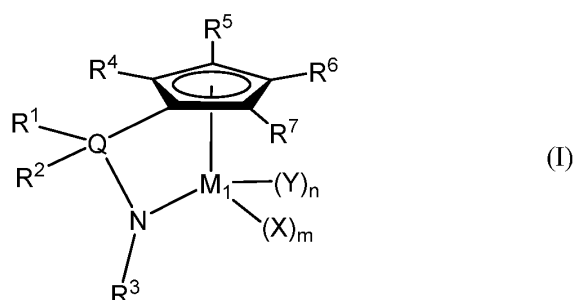
SUMMARY

[004] Embodiments of the present disclosure meet this need by combining catalysts derived from two different classes – constrained geometry metal–ligand complexes (CGC catalysts) and guanidine complexes (GD catalysts).

[005] Without being bound by theory, the weight average molecular weight of the polymer produced by GD catalysts is more sensitive to hydrogen than is the molecular weight of the polymer produced by CGC catalysts. Consequently, the molecular weight split (difference in molecular weight of the polyethylene produced by the two catalysts) can be tailored by adjusting hydrogen levels without significantly changing other conditions. Additionally, the amount of comonomer in the polymer produced by the CGC catalyst is higher than the amount of comonomer

in the polymer produced by the GD catalyst. This combination leads to the higher molecular weight fraction containing more comonomer than the lower molecular weight fraction.

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



BRIEF DESCRIPTION OF FIGURES

[007] FIG. 1 is a GPC chromatograph of the molecular weight distribution and the comonomer incorporation of three polymers. The polymers are produced with a guanidine catalyst at 5 mmol H₂, a CGC catalyst at 5 mmol H₂, and both a guanidine catalyst and a CGC-catalyst at 40 mmol H₂.

[008] FIG. 2 is a GPC chromatograph of the molecular weight distribution and the comonomer incorporation of three polymers. The polymers are produced with a guanidine catalyst at 10 mmol H₂, a CGC catalyst at 10 mmol H₂, and both a guanidine catalyst and a CGC-catalyst at 40 mmol H₂.

[0009] FIG. 3 is a GPC chromatograph of the molecular weight distribution and the comonomer incorporation of three polymers. The polymers are produced with a guanidine catalyst at 10 mmol H₂, a CGC catalyst at 10 mmol H₂, and both a guanidine catalyst and a CGC-catalyst at 40 mmol H₂.

DETAILED DESCRIPTION

[0010] 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.

[0011] Common abbreviations are listed below:

[0012] **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn** : benzyl; **i-Pr** : *iso*-propyl; **t-Bu** : *tert*-butyl; **t-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf** : trifluoromethane sulfonate; **THF** : tetrahydrofuran; **Et₂O** : diethyl ether; **CH₂Cl₂** : dichloromethane; **CV** : column volume (used in column chromatography); **EtOAc** : ethyl acetate; **C₆D₆** : deuterated benzene or benzene-*d*₆; **CDCl₃** : deuterated chloroform; **Na₂SO₄** : sodium sulfate; **MgSO₄** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi** : butyllithium; ***t*-BuLi** : *tert*-butyllithium; **Cu₂O** : Copper (I) Oxide; ***N,N'*-DMEDA** : *N,N'*-dimethylethylenediamine; **K₃PO₄** : Potassium phosphate tribasic; **Pd(AmPhos)Cl₂** : Bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II); **PdCl(crotyl)Amphos** : Chloro(crotyl)[di-*tert*-butyl(4-dimethylaminophenyl)phosphine]palladium(II); **Pd(dppf)Cl₂** : [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride; **AgNO₃** : Silver nitrate; **K₂CO₃** : potassium carbonate; **Cs₂CO₃** : cesium carbonate; ***i*-PrOBPin** : 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; **BrCl₂CCCl₂Br** : 1,2-dibromotetrachloroethane; **N₂** : nitrogen gas; **PhMe** : toluene; **PPR** : parallel pressure reactor; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **GC** : gas chromatography; **GPC** : gel permeation chromatography; **LC** : liquid chromatography; **NMR** : nuclear magnetic resonance; **MS** : mass spectrometry; **mmol** : millimoles; **mL** : milliliters; **M** : molar; **min or mins** : minutes; **h or hrs** : hours; **d** : days; **R_f** : retention fraction; **TLC** : thin-layered chromatography; **rpm** : revolution per minute; **LogM** : the log of the molecular weight; **dWf** : the change in the weight fraction; **dLogM** : the change in the log of the molecular weight; **M_w** : weight average molecular weight; **M_n** : number average molecular weight; **M_z** : z-average molar mass.

[0013] 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.

[0014] 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.

[0015] 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 .

[0016] 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.

[0017] The terms “halogen atom,” “halogen,” “halide,” “saturated,” “unsaturated,” ““(C₁–C₅₀)hydrocarbyl,” ““(C₁–C₅₀)alkyl,” ““(C₁–C₁₈)alkyl,” ““(C₆–C₅₀)aryl,” ““(C₃–C₅₀)cycloalkyl,” ““(C₁–C₅₀)alkylene,” “heteroatom,” and ““(C₁–C₅₀)heteroalkyl” are as defined in publication number WO2020185494A1.

[0018] The term “polymer” refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term “homopolymer,” usually employed to refer to polymers prepared from only one type of monomer as well as “copolymer” which refers to polymers prepared from two or more different monomers.

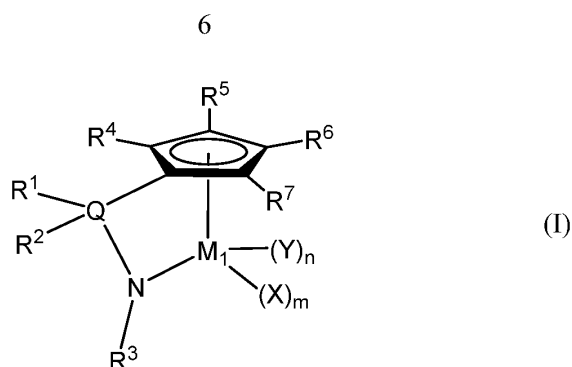
[0019] “Polyethylene” or “ethylene-based polymer” shall mean polymers comprising greater than 50% by weight of units which have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more comonomers). Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE); Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); single-site catalyzed Linear Low Density Polyethylene, including both linear and substantially linear low density resins (m-LLDPE); Medium Density Polyethylene (MDPE); and High Density Polyethylene (HDPE).

[0020] As used herein, “multimodal” refers to polymers produced from a plurality of polymer fractions, each polymer fraction being produced by a distinct catalyst. Multimodal may include bimodal polymers having two polymer fractions, trimodal ethylene-based polymers having three polymer fractions, or polymers having more than three polymer fractions.

[0021] Embodiments of this disclosure include process of producing ethylene-based polymers, the process comprising reacting ethylene and optionally one or more olefin monomers in one or more reactors in the presence of a catalyst system and optionally in the presence of hydrogen.

[0022] The catalyst system includes one or more constrained geometry procatalysts according to formula (I) and one or more guanidine procatalysts according to formula (II).

[0023] Embodiments of this disclosure include catalyst systems that include one or more constrained geometry procatalysts according to formula (I):



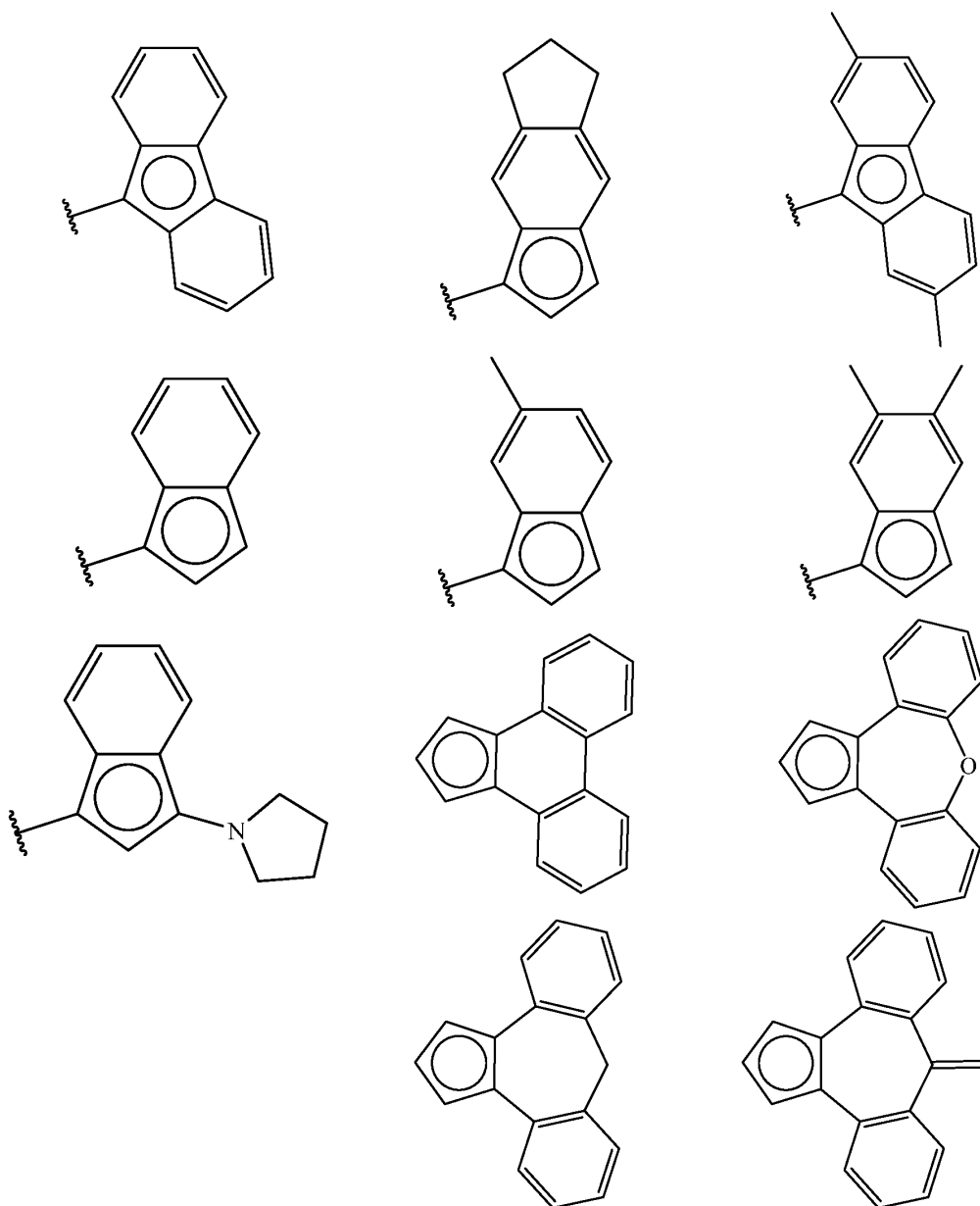
[0024] In formula (I), M_1 is titanium, zirconium, hafnium, or scandium; m is 1 or 2, n is 0, 1, or 2; and each X is a monodentate ligand independently chosen from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$, $-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, $-CH_2Ge(R^C)_{3-Q}(OR^C)_Q$, $-Ge(R^C)_{3-Q}(OR^C)_Q$, $-P(R^C)_{2-W}(OR^C)_W$, $-P(O)(R^C)_{2-W}(OR^C)_W$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^C Si(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$, $-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$, $-NHC(O)R^C$, $-C(O)N(R^C)_2$, $-C(O)NHR^C$, $-C(O)NH_2$, a halogen, $B(R^Y)_4$, $Al(R^Y)_4$, or $Ga(R^Y)_4$, or a hydrogen, wherein each R^C is independently a (C_1-C_{30}) hydrocarbyl, or (C_1-C_{30}) heterohydrocarbyl, and each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^Y is $-H$, (C_1-C_{30}) hydrocarbyl, or halogen atom, wherein two X ligands can be connected to form a ring. The metal–ligand complex is overall charge-neutral.

[0025] In formula (I), N is nitrogen; Q is carbon, silicon, or germanium; R^1 and R^2 are independently selected from $-H$, (C_1-C_{40}) hydrocarbyl, and (C_1-C_{40}) heterohydrocarbyl; and R^3 is independently selected from (C_1-C_{40}) hydrocarbyl, and (C_1-C_{40}) heterohydrocarbyl.

[0026] In formula (I), R^4 , R^5 , R^6 , and R^7 are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl wherein any of the R^4 , R^5 , R^6 , and R^7 optionally are connected to form a ring structure.

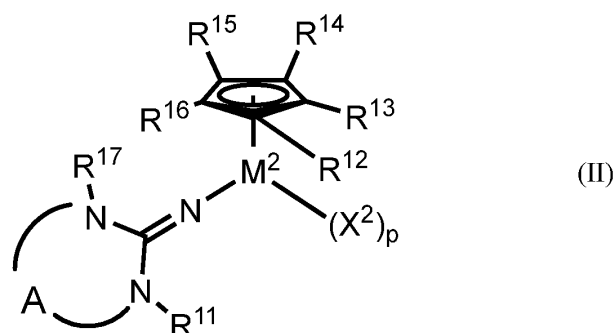
[0027] In one or more embodiments, in formula (I), R^1 and R^2 are methyl, ethyl, propyl, isopropyl, isobutyl, or phenyl. In some embodiments, R^3 is independently (C_1-C_{12}) alkyl. In various embodiments, R^4 , R^5 , R^6 , and R^7 are methyl; or R^4 and R^7 are methyl, or R^5 and R^6 are methyl or R^6 and R^7 are methyl. In some embodiments, R^6 is $-OMe$; or R^5 is $-NMe_2$.

[0028] In some embodiment, in formula (I), (A) R^4 and R^5 are connected and form a ring optionally substituted by one or more R^S ; or (B) R^6 and R^7 are connected and form a ring optionally substituted by one or more R^S ; or (C) both (A) and (B). Thus, when (A), (B), or (C) occurs, the cyclopentadienyl of formula (I) has a structure selected from the group consisting of:



[0029] Embodiments of this disclosure include catalyst systems that include one or more guanine procatalysts according to formula (II):

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[0030] In formula (II), M^2 is titanium, zirconium, or hafnium. Each X^2 is independently selected from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-CH_2Si(R^C)_{3-J}(OR^C)_J$, $-Si(R^C)_{3-J}(OR^C)_J$, $-OSi(R^C)_{3-J}(OR^C)_J$, $-CH_2Ge(R^C)_{3-J}(OR^C)_J$, $-Ge(R^C)_{3-J}(OR^C)_J$, $-P(R^C)_{2-K}(OR^C)_K$, $-P(O)(R^C)_{2-K}(OR^C)_K$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^CSi(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$, $-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$, $-NHC(O)R^C$, $-C(O)N(R^C)_2$, $-C(O)NHR^C$, $-C(O)NH_2$, 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 J is 0, 1, 2 or 3, and each K is 0, 1, or 2; each R^Y is $-H$, (C_1-C_{30}) hydrocarbyl, or halogen atom, wherein two X^2 ligands can be connected to form a ring.

[0031] In formula (II), subscript p is 1 or 2. In some embodiments, p is 2. N is nitrogen. R^{11} and R^{17} are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{30}) aryl, or (C_5-C_{30}) heteroaryl. R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} are each independently (C_1-C_{12}) alkyl, halogen substituted (C_1-C_{12}) alkyl, halogen substituted (C_6-C_{18}) aryl, halogen substituted (C_3-C_{50}) cycloalkyl, or $-H$.

[0032] In formula (II), A is $-C(R^8)C(R^9)-$, $-CH(R^8)CH(R^9)-$, or $-CH(R^8)CH(R^9)CH(R^{10})-$. R^8 , R^9 , and R^{10} are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{30}) aryl, or (C_5-C_{30}) heteroaryl. R^{17} and R^8 may be connected to form an aromatic or non-aromatic ring; or R^8 and R^9 may be connected to form an aromatic or non-aromatic ring; or when A is $-C(R^8)C(R^9)C(R^{10})-$, R^9 and R^{10} may be connected to form an aromatic or non-aromatic ring, or R^{10} and R^{11} may be connected to form an aromatic or non-aromatic ring; or when A is $-C(R^8)C(R^9)-$, R^9 and R^{11} may be connected to form an aromatic or non-aromatic ring.

[0033] In some embodiments, in formula (II), A is $-C(R^8)C(R^9)-$ and R^8 and R^9 are independently (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{30}) aryl, or

(C₅–C₃₀)heteroaryl, as defined hereinabove. In various embodiments, in formula (II), A is –C(R⁸)C(R⁹)C(R¹⁰)– and R⁸ and R⁹ are independently (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₃₀)aryl, or (C₅–C₃₀)heteroaryl, as defined hereinabove. In one or more embodiments, R⁸, R⁹, and R¹⁰ are (C₁–C₂₀)alkyl or –H, and R¹¹ and R¹⁷ are substituted (C₆–C₁₈)aryl. In some embodiments, in formula (II) one of R⁸, R⁹, and R¹⁰ is selected from –OMe and –NMe₂.

[0034] In various embodiments, in formula (II), R⁸, R⁹, and R¹⁰ are independently selected from the group consisting of: methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, dimethylamino, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0035] In one or more embodiments, R¹⁷ and R¹¹ are phenyl substituted with one or more R^S, where R^S is (C₁–C₁₂)alkyl. In some embodiments, R¹⁷ and R¹¹ is 2,4,6-trimethylphenyl or di-*iso*-propylphenyl.

[0036] In one or more embodiments, R¹², R¹³, R¹⁴, R¹⁵, or R¹⁶ are –H, –CF₃ (C₁–C₁₂)alkyl or (C₆–C₁₂)aryl or fluoro-substituted phenyl. In some embodiments, R¹², R¹³, R¹⁴, R¹⁵, or R¹⁶ are selected from the group consisting of methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, dimethylamino, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

[0037] In the metal–ligand complex according to formula (I), each Y bonds with M₁ 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 M₁, 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 a unsaturated hydrocarbon. Examples of neutral heterohydrocarbon Lewis bases includes, but are not limited to, amines, trialkylamines, ethers, cycloethers, or sulfides. An example of anionic hydrocarbon includes, but is not limited to, cyclopentadienyl. An example of a neutral hydrocarbon Lewis Base includes, but is not limited to, 1,3-buta-di-ene.

[0038] In some embodiments, the Lewis base is (C₁–C₂₀)hydrocarbon. In some embodiments, the Lewis base is cyclopentadiene or 1,3-buta-di-ene. In various embodiments, the Lewis base is

(C₁–C₂₀)heterohydrocarbon, wherein the hetero atom of the heterohydrocarbon is oxygen. In some embodiments, Y is tetrahydrofuran, diethyl ether, or methyl *tert*-butyl ether (MTBE).

[0039] Additionally in formula (I), each X and each Y can be a monodentate ligand that, independently from any other ligands X and Y, is a halogen, unsubstituted (C₁–C₂₀)hydrocarbyl, unsubstituted (C₁–C₂₀)hydrocarbylC(O)O–, or R^KR^LN–, 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), X is benzyl, chloro, –CH₂SiMe₃, or phenyl.

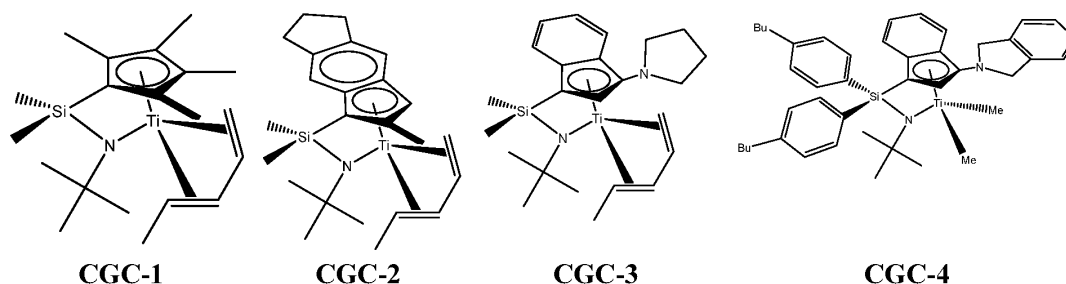
[0040] In further embodiments, each X and/or each Y is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments, each X is the same. In other embodiments, at least two X are different from each other. In the embodiments in which at least two X are different from each other, at least one X is methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In further embodiments, the bidentate ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0041] In some embodiments, any or all of the chemical groups (e.g., X and R¹–R⁷) 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–R⁷ 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 the 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–R⁷ 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.

[0042] As stated hereinabove, the weight average molecular weight of the polymer produced by GD catalysts is more sensitive to hydrogen than is the molecular weight of the polymer produced by CGC catalysts. Consequently, the molecular weight split (difference in molecular weight of the polyethylene produced by the two catalysts) can be tailored by adjusting hydrogen levels without significantly changing other conditions. Additionally, the amount of comonomer

in the polymer produced by the CGC catalyst is higher than the amount of comonomer in the polymer produced by the GD catalyst under the same conditions. This combination leads to the higher molecular weight fraction containing more comonomer than the lower molecular weight fraction.

[0043] In illustrative embodiments, the catalyst systems may include a metal–ligand complex according to formula (I) having the structure of any of the procatalyst CGC-1, CGC-2, CGC-3, or CGC-4:



[0044] Cocatalyst Component

[0045] The catalyst system comprising a metal–ligand complex of formula (I) and formula (II) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, the procatalyst according to a metal–ligand complex of formulas (I) and (II) 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 formulas (I) and (II) include both a procatalyst form, which is neutral, and a catalytic form, which may be positively charged due to the loss of a monoanionic ligand, such a benzyl or phenyl. Suitable activating co-catalysts for use herein include alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0046] 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 scavenging agent sequesters impurities in the reactor prior to addition of the procatalyst, and as such, does not constitute an activator. 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. 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.

[0047] 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.

[0048] 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)hydrocarbenium borate (e.g. trityl tetrafluoroborate) or a tri((C₁–C₂₀)hydrocarbyl)ammonium tetra(C₁–C₂₀)hydrocarbyl)borate (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borate). 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.

[0049] 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.

[0050] The catalyst system that includes the metal–ligand complex of formulas (I) and (II) 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)methylammonium tetrakis(pentafluorophenyl)borate, and combinations thereof.

[0051] In some embodiments, more than one of the previously mentioned activating co-catalysts may be used in combination with each other. A specific example of a co-catalyst combination is a mixture of a tri((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 formulas (I) and (II) to total number of moles of one or more of the activating co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some other embodiments, at least 1: 1000; and 10:1 or less, and in some other embodiments, 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, the number of moles of the alumoxane that are employed is at least 25 times the number of moles of the metal–ligand complex of formulas (I) and (II). When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, in some other embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal–ligand complexes of formulas (I) and (II) from 0.5: 1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal–ligand complexes of formulas (I) and (II).

[0052] Polymerization Process

[0053] Embodiments of this disclosure include process of producing ethylene-based polymers, the process comprising reacting ethylene and optionally one or more olefin monomers in one or more reactors in the presence of a catalyst system and optionally in the presence of hydrogen. In some embodiments, the process occurs in the presence of hydrogen. In one or more embodiments, the amount of hydrogen may be greater than 0 mmol. In embodiments, the amount of hydrogen may range from greater than 0 mmol to less than or equal to 1,000 mmol. In embodiments, the amount of hydrogen may range from greater than 0 mmol to less than or equal to 500 mmol, from greater than 0 mmol to less than or equal to 100 mmol, or from greater than 0 mmol to less than or equal to 10 mmol. In some embodiments, the hydrogen amount in mol%, which is the molar feed rate of fresh hydrogen / molar feed rate of fresh ethylene * 100, is from greater than 0.0 mol% to 4 mol%.

[0054] Any conventional polymerization processes may be employed to produce the polyolefin composition according to the present disclosure. Such conventional polymerization processes include, but are not limited to, solution polymerization process, particle forming polymerization process, and combinations thereof using one or more conventional reactors e.g. loop reactors, isothermal reactors, fluidized bed reactors, stirred tank reactors, batch reactors in parallel, series, and/or any combinations thereof. In various embodiments, the polymerization process is a solution polymerization reaction.

[0055] 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.

[0056] 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.

[0057] 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.

[0058] Polyolefins

[0059] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene-based polymers. In some embodiments, there is only ethylene in the polymerization scheme, creating an ethylene homopolymer. However, additional α -olefins may be incorporated into the polymerization procedure. The additional α -olefin co-monomers typically have no more than 20 carbon atoms. For example, the α -olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α -olefin co-monomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. For example, the one or more α -olefin co-monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene.

[0060] The ethylene-based polymers may comprise at least 60 weight percent monomer units derived from ethylene; at least 70 weight percent monomer units derived from ethylene; at least 80 weight percent monomer units derived from ethylene; or from 50 to 100 weight percent monomer units derived from ethylene; or from 80 to 100 weight percent units derived from ethylene. In some embodiments, the ethylene-based polymers may comprise at least 90 mole

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

[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] 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.

[0063] The ethylene-based polymer may have a density according to ASTM D792 (incorporated herein by reference in its entirety) from 0.850 g/cm^3 to 0.970 g/cm^3 , from 0.880 g/cm^3 to 0.920 g/cm^3 , from 0.880 g/cm^3 to 0.910 g/cm^3 , or from 0.880 g/cm^3 to 0.900 g/cm^3 , for example.

[0064] 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.

[0065] Gel Permeation Chromatography (GPC)

[0066] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 160° Celsius and the column and detector compartment were set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0067] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{\text{polyethylene}} = A \times (M_{\text{polystyrene}})^B \quad (\text{EQ1})$$

[0068] In equation 1, M is the molecular weight, A has a value of 0.413 and B is equal to 1.0.

[0069] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[0070] 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.

[0071] 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.

[0072] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

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

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

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

[0073] 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.

[0074] $\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)})$ (EQ5)

[0075] IR5 GPC Octene Composition Calibration

[0076] A calibration for the IR5 detector rationing was performed using at least ten ethylene-based polymer standards (Octene as comonomer) made by single-site metallocene catalyst from a single reactor in solution process (polyethylene homopolymer and ethylene/octene copolymers) of a narrow SCB distribution and known comonomer content (as measured by ^{13}C NMR Method, Qiu et al., Anal. Chem.2009, 81, 8585–8589), ranging from homopolymer (0 SCB/1000 total C) to approximately 40 SCB/1000 total C, where total C = carbons in backbone + carbons in branches. Each standard had a weight-average molecular weight from 36,000 g/mole to 126,000 g/mole measured by GPC. Each standard had a molecular weight distribution (Mw/Mn) from 2.0 to 2.5. Polymer properties for the SCB standards are shown in Table A.

Table A: “Copolymer” Standards

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

[0077] 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:

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

[0078] In Equation 6, 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.

[0079] Chain transfer constant calculations

[0080] 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.

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

EXAMPLES

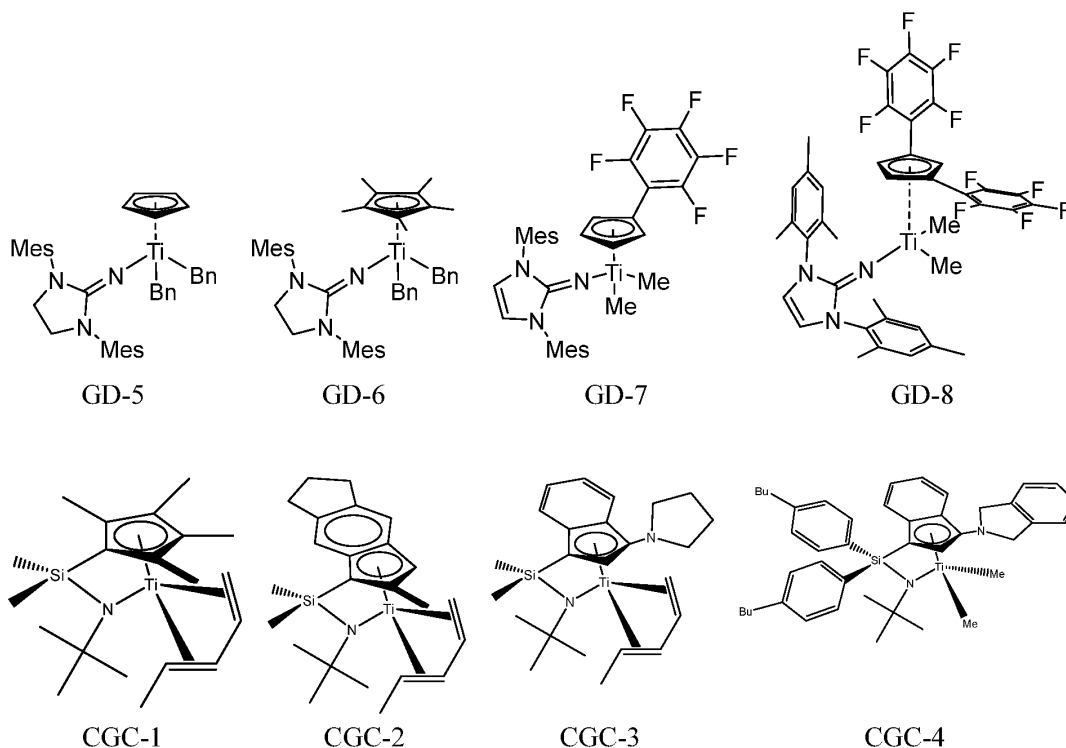
[0081] One or more features of the present disclosure are illustrated in view of the examples as follows:

GD-1

GD-2

GD-3

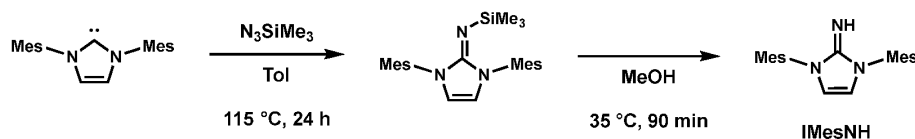
GD-4



[0082] Synthetic Protocols

[0083] All commercial chemicals were used without further purification. All syntheses were performed in a continuous nitrogen purge glovebox unless otherwise stated. (Cyclopentadienyl)titanium(IV) tribenzyl (CpTiBn_3) was prepared by the reaction of 3 equivalents of benzylmagnesium chloride with one equivalent of (cyclopentadienyl)titanium(IV) trichloride. (Pentamethylcyclopentadienyl)titanium(IV) tribenzyl (Cp^*TiBn_3) was prepared by the reaction of 3 equivalents of benzylmagnesium chloride with one equivalent of (pentamethylcyclopentadienyl)titanium(IV) trichloride.

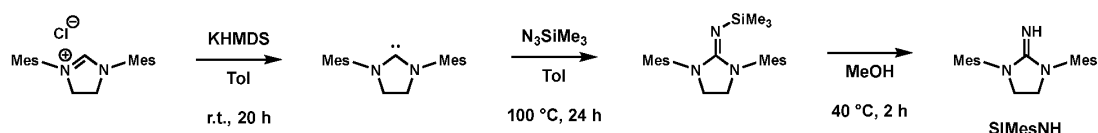
[0084] Synthesis of 1,3-dimesitylimidazol-2-imine (IMesNH)



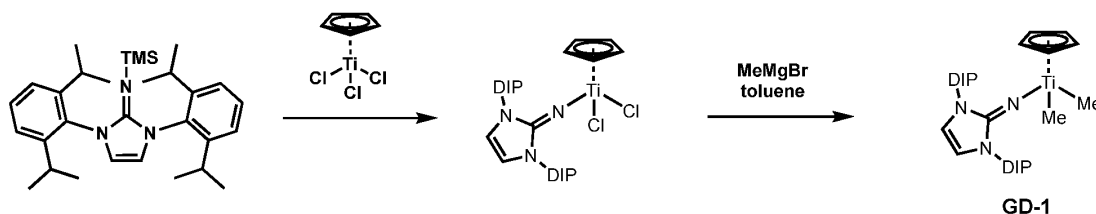
[0085] In a nitrogen purge glovebox, 1,3-di-mesityl-imidazol-2-ylidene (1.13 g, 3.71 mmol, 1 equiv) was dissolved in toluene at ambient temperature. After stirring for 5 min, trimethylsilylazide (0.69 mL, 5.20 mmol, 1.4 equiv) was added dropwise. The reaction mixture

was heated to 115 °C and stirred for 24 h. The reaction was cooled to ambient temperature, filtered through a PTFE filter syringe, and concentrated. The residue was triturated with hexanes (2 x 2 mL) and dried in vacuo. The resulting solid was combined with methanol (2.25 mL, 15 equiv) and stirred at 35 °C for 90 min. The volatiles were removed in vacuo and the resulting crude material was then triturated with hexanes (2 x 4 mL), washed with warm (35 °C) hexanes (75 mL), and dried under vacuum. Yield: 0.560 g, 47%. ¹H NMR (400 MHz, C₆D₆) δ 6.77 (s, 4H), 5.72 (s, 2H), 4.28 (s, 1H), 2.24 (s, 12H), 2.12 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 151.7, 137.7, 137.2, 134.3, 129.2, 112.0, 20.8, 17.9.

[0086] Synthesis of 1,3-dimesitylimidazolidin-2-imine (SIMesNH)

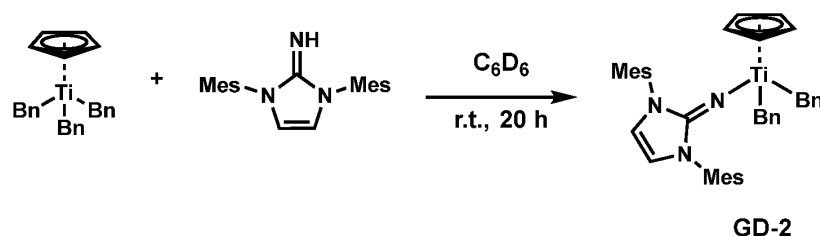


[0087] In a nitrogen purge glovebox, 1,3-dimesityl-4,5-dihydro-1H-imidazolinium chloride (1.055 g, 3.08 mmol, 1 equiv) was suspended in toluene (40 mL) at ambient temperature. After stirring for 5 min, KHMDS (0.644 g, 3.23 mmol, 1.05 equiv) was added directly as a solid and the resulting mixture was stirred at ambient temperature for 20 h. The reaction mixture was then filtered through CELITE and the filtrate was concentrated in vacuo. The resulting residue was triturated with hexanes (2 x 5 mL) and then extracted into warm (35 °C) hexanes (60 mL) and filtered. The filtrate was concentrated and stored at -25 °C for 48 h. The precipitate was collected by filtration and dried under vacuum. The solid was dissolved in toluene (30 mL) at ambient temperature and then excess trimethylsilylazide (0.57 mL, 4.31 mmol, 1.4 equiv) was added dropwise. The resulting mixture was heated at 100 °C for 24 h and then filtered. The volatiles were removed in vacuo and the resulting residue was triturated with hexanes (2 x 2 mL). The material was then combined with methanol (2 mL) and stirred at 40 °C for 2 h. The volatiles were removed in vacuo and the residue was triturated with hexanes (2 x 2 mL), washed with hexanes (2 x 4 mL), and dried under vacuum. Yield: 0.440 g, 45%. ¹H NMR (400 MHz, C₆D₆) δ 6.80 (s, 4H), 4.44 (s, 1H), 3.24 (s, 4H), 2.29 (s, 12H), 2.14 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 156.8, 138.1, 137.1, 129.7, 45.7, 21.0, 18.1.

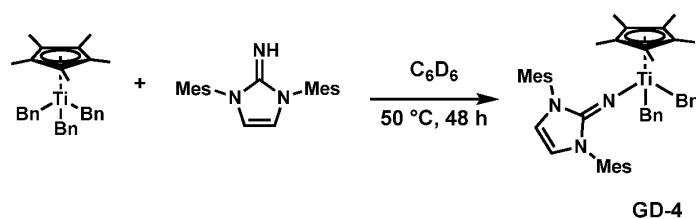
[0088] Synthesis of GD-1

[0089] Step 1: In a N₂ atmosphere glove box, to a 40-mL vial equipped with a stir bar, was added 1,3-bis(2,6-diisopropylphenyl)-N-trimethylsilyl-imidazol-2-imine (0.300 g, 0.631 mmol) and trichloro(cyclopenta-2,4-dien-1-yl)titanium (0.138 g, 0.631 mmol) in 5 mL of dry degassed toluene. The vial was fitted with a small reflux condenser then the orange-yellow colored reaction mixture was heated at 80 °C for 3 hours. Everything solubilized at elevated temperature. After this time the reaction was cooled to room temperature then 20 mL of pentane was added. The vial was placed in a freezer (−35 °C) for 6 days, but could have been overnight. The yellow precipitate was isolated by filtration and washed with cold pentane (3 x 5 mL). The resulting yellow solid was dried under vacuum to provide [[1,3-bis(2,6-diisopropylphenyl)23midazole-2-ylidene]amino]-dichloro-cyclopenta-2,4-dien-1-yl-titanium (0.321 g, 0.547 mmol, yield: 87 %): ¹H NMR (400 MHz, benzene-d₆) δ 7.24 (dd, J = 8.5, 6.9 Hz, 2H), 7.13 (d, J = 1.0 Hz, 2H), 5.93 (s, 4H), 5.76 (s, 2H), 2.94 (hept, J = 6.8 Hz, 4H), 1.49 (d, J = 6.8 Hz, 12H), 1.07 (d, J = 6.9 Hz, 12H).

[0090] Step 2: In a N₂ atmosphere glove box to a 40-mL vial equipped with a stir bar was added [[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]amino]-dichloro-cyclopenta-2,4-dien-1-yl-titanium (0.300 g, 0.512 mmol) and 10 mL of dry degassed toluene. The vial was placed in a freezer (−35 °C) for 15 minutes, after which time bromo(methyl)magnesium (3.00 mol/L, 0.358 mL, 1.07 mmol) was added slowly to the red suspension. The mixture tended towards yellow/brown with a small amount of precipitate. The reaction mixture was stirred at room temperature for 2 hours then after this time the reaction was concentrated to dryness. The material was taken up in toluene/pentane (15 mL, 4:1) then passed through a CELITE plug. The plug was further extracted with toluene/pentane (10 mL, 4:1). The combined yellow organic layers were concentrated to dryness to provide GD-1 (0.240 g, 0.440 mmol, yield: 86%) as a yellow powder; ¹H NMR (400 MHz, benzene-d₆) δ 7.22 (dd, J = 8.6, 6.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 4H), 5.89 (s, 2H), 5.73 (s, 5H), 3.24 – 3.09 (m, J = 6.6 Hz, 4H), 1.39 (d, J = 6.8 Hz, 12H), 1.15 (d, J = 6.9 Hz, 12H), 0.21 (s, 6H).

[0091] Synthesis of GD-2

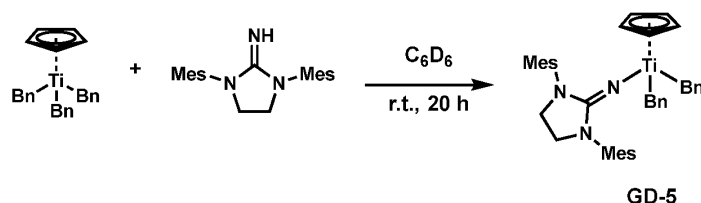
[0092] Inside a nitrogen purge glovebox, CpTiBn₃ (50 mg, 0.13 mmol, 1 equiv) was combined with C₆D₆ (0.4 mL) and a stir bar. The mixture was allowed to stir at ambient temperature for 5 min until all the material had dissolved, affording a deep red solution. Separately, IMesNH (41 mg, 0.13 mmol, 1 equiv) was dissolved in C₆D₆ (0.3 mL). The nearly colorless solution of ligand was then added dropwise to the Ti-containing solution at ambient temperature while stirring. An additional ~0.3 mL of C₆D₆ was used to extract and transfer any residual ligand from its original vial to the reaction mixture. The resulting dark red-brown and homogeneous mixture was allowed to continue stirring at ambient temperature for 20 h. After this time, the reaction mixture was concentrated to an orange-red residue that was then triturated with hexanes (2 x 2 mL) and dried under vacuum. The material was taken up in toluene (2 mL), filtered, and concentrated to half the volume. Hexanes was added to the concentrated toluene solution causing mild turbidity. The contents of the vial were mixed thoroughly and then stored at -25 °C for 24 h. The precipitated material was collected and dried in vacuo. Yield: 74 mg, 93 %. ¹H NMR (400 MHz, C₆D₆) δ 7.19 – 7.12 (m, overlapping with NMR solvent, 4H) 6.86 (tt, *J* = 7.2, 1.3 Hz, 2H), 6.77 (s, 4H), 6.72 (d, *J* = 7.3 Hz, 4H), 5.59 (s, 2H), 5.48 (s, 5H), 2.45 (d, *J* = 9.1 Hz, 2H), 2.21 (s, 12H), 2.18 (d, *J* = 9.2 Hz, 2H), 2.08 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 153.1, 142.0, 139.4, 136.8, 133.5, 129.5, 126.3, 120.3, 113.4, 113.1, 70.8, 21.0, 18.1.

[0093] Synthesis of GD-4

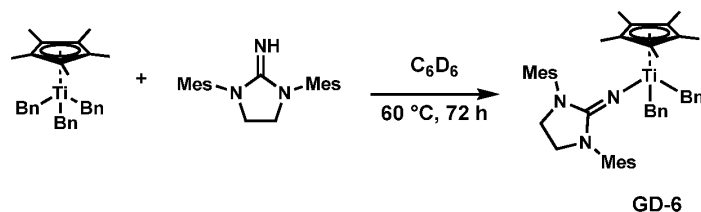
[0094] Inside a nitrogen purge glovebox, Cp*TiBn₃ (50 mg, 0.11 mmol, 1 equiv) was combined with C₆D₆ (0.4 mL) and a stir bar. The mixture was allowed to stir at ambient temperature for 5 min until all the material had dissolved, affording a deep red solution.

Separately, IMesNH (35 mg, 0.11 mmol, 1 equiv) was dissolved in C₆D₆ (0.3 mL). The nearly colorless solution of ligand was then added dropwise to the Ti-containing solution at ambient temperature while stirring. An additional ~0.3 mL of C₆D₆ was used to extract and transfer any residual ligand from its original vial to the reaction mixture. The dark red reaction mixture was then heated at 50 °C for 48 h to achieve full conversion to the desired product. The volatiles were removed in vacuo, affording an orange-red residue that was then triturated with hexanes (2 x 2 mL) and dried under vacuum. The material was taken up in toluene (1.5 mL), filtered, and concentrated to half the volume. Hexanes (0.5 mL) was added and the contents of the vial were mixed thoroughly prior to storage at -25 °C for 24 h. The resulting orange precipitate was collected by decanting the mother liquor, rinsing with cold hexanes (1 mL), and drying in vacuo. Yield: 71 mg, 95 %. ¹H NMR (500 MHz, C₆D₆) δ 7.21 (dd, *J* = 8.5, 6.9 Hz, 4H), 6.92 (t, *J* = 7.9 Hz, 6H), 6.73 (s, 4H), 5.58 (s, 2H), 2.28 (s, 12H), 2.21 (d, *J* = 10.5 Hz, 2H), 2.10 (s, 6H), 1.74 (d, *J* = 10.5 Hz, 2H), 1.60 (s, 15H). ¹³C NMR (126 MHz, C₆D₆) δ 153.4, 141.5, 138.9, 136.9, 133.9, 129.5, 120.7, 120.3, 113.3, 73.1, 21.0, 18.8, 11.7.

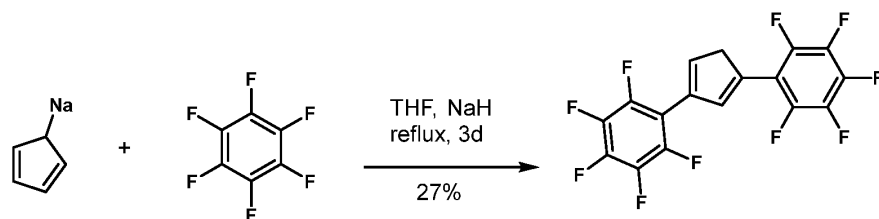
[0095] Synthesis of GD-5



[0096] Inside a nitrogen purge glovebox, CpTiBn₃ (50mg, 0.13 mmol, 1 equiv) combined with C₆D₆ (0.4 mL) and a stir bar, affording a deep red solution. Separately, SIMesNH ligand (42 mg, 0.13 mmol, 1 equiv) was dissolved in C₆D₆ (0.4 mL), affording a pale-yellow solution. The solution of ligand was then added dropwise to the stirring solution of Ti precursor at ambient temperature. Additional C₆D₆ (0.2 mL) was used to extract and transfer all the ligand material from its vial into the reaction vial. There were no noticeable color or turbidity changes upon addition of ligand to metal. The reaction mixture was allowed to stir at ambient temperature for 20 h. The volatiles were removed in vacuo, affording a red residue. The residue was triturated with hexanes (2 x 2 mL) and dried under vacuum, affording a free-flowing red-orange solid. Yield: 77 mg, 96.6%. ¹H NMR (400 MHz, C₆D₆) δ 7.17 – 7.12 (m, overlapping with NMR solvent peak, 4H), 6.90 – 6.82 (m, 2H), 6.78 (s, 4H), 6.66 (dd, *J* = 8.2, 1.3 Hz, 4H), 5.45 (s, 5H), 3.17 (s, 4H), 2.34 (d, *J* = 9.6 Hz, 2H), 2.32 (s, 12H), 2.13 (d, *J* = 9.1 Hz, 2H), 2.08 (s, 6H). ¹³C NMR (101 MHz, C₆D₆) δ 152.8, 148.3, 138.3, 137.6, 134.9, 129.7, 126.2, 120.5, 113.8, 72.8, 45.4, 21.0, 18.1.

[0097] Synthesis of GD-6

[0098] (Inside a nitrogen purge glovebox, Cp*TiBn₃ (50mg, 0.11 mmol, 1 equiv) was combined with C₆D₆ (0.4 mL) and a stir bar, affording a medium-red colored solution. Separately, SIMesNH ligand (35 mg, 0.11 mmol, 1 equiv) was dissolved in C₆D₆ (0.4 mL), affording a pale-yellow solution. The solution of ligand was then added dropwise to the stirring solution of Ti precursor at ambient temperature. Additional C₆D₆ (0.2 mL) was used to extract and transfer all the ligand material from its vial into the reaction vial. NMR monitoring revealed that metalation did not occur at ambient temperature. The reaction mixture was heated progressively and found to require heating at 60 °C for conversion. After 72 h at 60 °C, the volatiles were removed in vacuo, affording in a red residue. The residue was triturated with hexanes (2 x 2 mL) and then washed with hexanes (1 x 2 mL) affording a free-flowing, red-orange solid. Yield: 46 mg, 61 %. ¹H NMR (400 MHz, C₆D₆) δ 7.19 (t, *J* = 7.7 Hz, 4H), 6.97 – 6.88 (m, 2H), 6.85 – 6.80 (m, 4H), 6.75 (s, 4H), 3.22 (s, 4H), 2.43 (s, 12H), 2.21 (d, *J* = 10.4 Hz, 2H), 2.12 (s, 6H), 1.73 (d, *J* = 10.4 Hz, 2H), 1.60 (s, 15H). ¹³C NMR (101 MHz, C₆D₆) δ 153.0, 147.4, 137.8, 137.7, 135.5, 129.7, 127.1, 121.0, 120.9, 74.6, 45.8, 21.0, 18.8, 11.8.

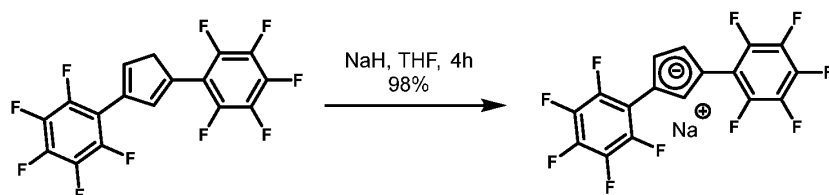
[0099] Synthesis of 6,6'-(cyclopenta-1,3-diene-1,3-diyl)bis(1,2,3,4,5-pentafluorobenzene)

[00100] A 250 mL round bottom flask was charged with Sodium Cyclopentadienylide (2.4 M in THF, 9.6 mL, 2.0 g, 0.023 mmol, 1 equiv), NaH (1.1 g, 0.046 mol, 2 equiv), C₆F₅ (42 g, 0.23 mol, 10 equiv), THF (100 mL), and a magnetic stir bar and the reaction mixture was refluxed under nitrogen for 3 d. The solvent was then removed under reduced pressure, and the residue was washed with pentane (3 × 50 mL). Pentane (100 mL) and water (20 mL) were added, the layers were separated, and the organic layer was dried over Na₂SO₄, filtered through neutral alumina,

and evaporated to afford white solid. The white solid was dissolved in 50 mL hot ethanol and recrystallized to obtain needle shaped white crystals (2.5g, 27%).

[00101] ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.28 (m, 2H), 4.05 (p, J = 1.7 Hz, 2H). ^{19}F NMR (471 MHz, CDCl_3) δ -139.78 – -140.00 (m, 4H), -156.42 (t, J = 20.8 Hz, 2H), -162.55 (td, J = 21.1, 6.9 Hz, 4H).

[00102] Synthesis of (2,4-bis(perfluorophenyl)cyclopenta-2,4-dien-1-yl)sodium



[00103] In a N_2 -filled glovebox, a 20 mL vial was charged with 6,6'-(cyclopenta-1,3-diene-1,3-diyl)bis(1,2,3,4,5-pentafluorobenzene) (500 mg, 1.25 mmol, 1 equiv), NaH (90 mg, 3.0 mmol, 3 equiv), 10 mL of dry THF, and a magnetic stir bar. Addition of NaH caused changed in color of the reaction mixture from colorless to yellow. The reaction mixture was stirred at ambient temperature for 4h. Solvent was evaporated under reduced pressure to obtain faint yellow solid material. To the solid material, 10 mL of hexanes were added and filtered the solid to obtain solid residue which was then dried under vacuum to obtain white powder (125 mg, 98%).

[00104] ^1H NMR (400 MHz, Benzene- d_6) δ 7.45 (p, J = 2.6 Hz, 1H), 6.95 (qd, J = 2.7, 1.7 Hz, 2H). ^{19}F NMR (376 MHz, C_6D_6) δ -144.91 – -145.54 (m), -165.81 – -166.41 (m), -168.34 (t, J = 21.7 Hz).

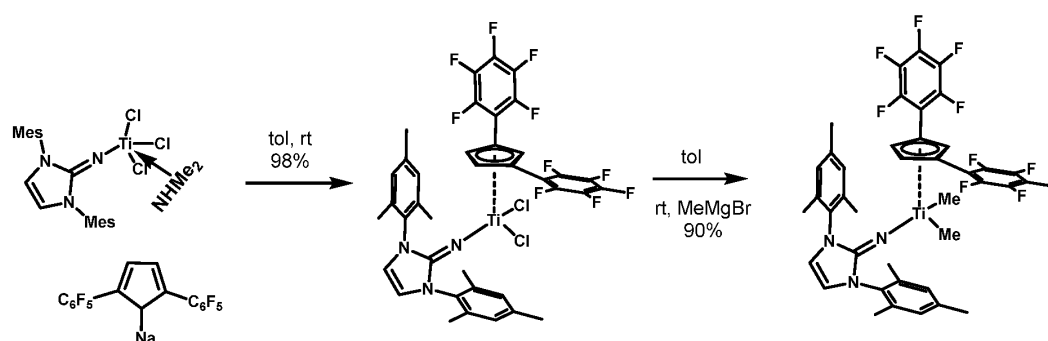
[00105] Synthesis of IMesN(Me₂NH)TiCl₃



[00106] In a nitrogen filled glovebox, $(\text{Me}_2\text{N})\text{TiCl}_3$ (54 mg, 0.27 mmol, 1 equiv) was added to a 7 mL glass vial with Et_2O (8 mL) and a magnetic stir bar at ambient temperature. The mixture was allowed to stir at ambient temperature for 15 min. In a separate vial, (IMesNH) ligand (87 mg, 0.27 mmol, 1 equiv) was combined with Et_2O (6 mL). The faint yellow solution of ligand was then added dropwise at ambient temperature to the stirring solution of Ti precursor, causing a color change to bright red-orange along with an increase in turbidity. The heterogeneous red-

orange suspension was then allowed to continue stirring at ambient temperature for 20 h. The bright orange solid was collected on a disposable frit, washed with Et₂O (2 x 4 mL) and pentane (2 x 3 mL). The orange solid further dried under vacuum and then stored at -25 °C. Yield: 0.100 g, 70 %. ¹H NMR (500 MHz, C₆D₆) δ 6.82 (s, 4H), 5.37 (s, 2H), 2.75 (br s, 1H), 2.20 (s, 12H), 2.09 (s, 6H), 1.96 (s, 6H). ¹³C NMR (126 MHz, C₆D₆) δ 140.3, 136.3, 131.5, 129.7, 128.4, 114.5, 21.1, 18.0.

[00107] Synthesis of GD-8



[00108] In a N₂-filled glovebox, a 20 mL vial was charged with IMesN(Me₂NH)TiCl₃ adduct (88 mg, 0.17 mmol, 1 equiv.), and 6 mL toluene was added. The sodium salt of the ligand (71.4 mg, 0.17 mmol, 1 equiv.) was dissolved in 7 mL toluene in another 20 mL vial. The Ti-precursor solution was added dropwise slowly to the sodium salts of the bis-C₆F₅Cp ligand at room temperature. The color of the reaction mixture changed from white to reddish orange. The reaction was stirred for 2 hours at ambient temperature. The solvent was removed under vacuum. The solid insoluble yellow material was washed with 2:1 toluene:hexane (10 mL) thrice. The residue was filtered through a fritted funnel to obtain orange powder which was dried under vacuum to afford the Ti-Cl₂ complex as an orange powder (140 mg, 98%).

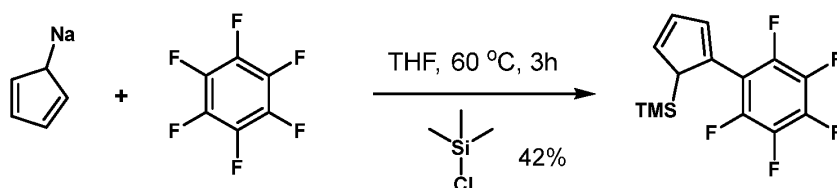
[00109] ¹H NMR (500 MHz, C₆D₆) δ 7.42 (s, 1H), 6.83 (s, 4H), 6.17 (s, 2H), 5.38 (s, 2H), 2.15 (d, J = 9.7 Hz, 18H). ¹⁹F NMR (471 MHz, C₆D₆) δ -139.36 (d, J = 23.8 Hz), -156.67 (t, J = 21.7 Hz), -163.60 (t, J = 24.4 Hz).

[00110] In a N₂-filled glovebox, a 20 mL vial was charged with the Ti-Cl₂ complex (80 mg, 0.095 mmol, 1 equiv), 5 mL of toluene, and a stir bar. To the solution, MeMgBr in hexanes (0.076 mL of 3 (M) MeMgBr in hexanes, 0.23 mmol, 2.4 equiv) was added and the reaction mixture was stirred for 30 min at ambient temperature. The color of the reaction changes from orange to dark yellow upon addition of MeMgBr. The solution was filtered through a fritted funnel and a yellowish orange filtrate was obtained. The filtrate was evaporated under vacuum to obtain a light-

yellow solid. To the light-yellow solid, 2 mL of toluene was added to dissolve the solid followed by addition of 10 mL of hexanes. The slurry was filtered through a fritted funnel to obtain a light-yellow filtrate. The solvent was removed to afford GD-8 as a light-yellow solid (68 mg, 90%).

[00111] ^1H NMR (400 MHz, C_6D_6) δ 7.59 – 7.52 (m, 1H), 6.80 (s, 4H), 5.89 (s, 2H), 5.55 (s, 2H), 2.15 (d, J = 9.6 Hz, 18H), 0.06 (s, 6H). ^{19}F NMR (376 MHz, C_6D_6) δ -62.32 – -243.56 (m).

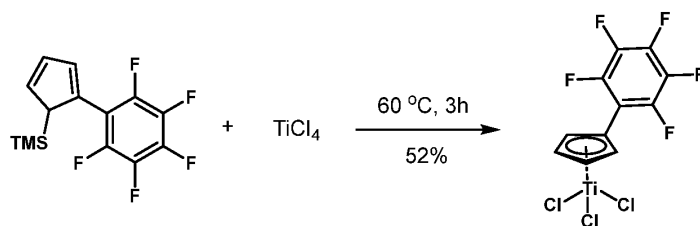
[00112] **Synthesis of a TMS-Cp-C₆F₅ Precursor**



[00113] In a N_2 -filled glovebox, a 100 mL round bottom flask was containing sodium cyclopentadiene (2M) THF solution (25 mL, 50 mmol, 1 equivalents) was added a solution of hexafluorobenzene (2.9 mL, 25 mmol, 0.5 equivalents) in 3 mL of THF dropwise over 5 mins. The dark green colored solution was heated to 60 °C for 3 hs. Chlorotrimethylsilane (4.4 mL, 0.035 mmol, 0.7 equiv) was added slowly over 5 mins, then stirred under N_2 overnight. The volatiles were removed under vacuum, the solid was triturated twice with 10 mL of hexane, filtered, and then washed with hexane (5x3 mL). Hexane was removed under vacuum yielding a brown liquid which was distilled under full vacuum at 115 °C. A clear colorless liquid was obtained (3.2 g, 42%).

[00114] ^1H NMR (500 MHz, C_6D_6) δ 6.94 – 6.34 (m, 3H), 3.55 – 2.82 (m, 1H), 0.21 – 0.12 (m, 1H), -0.13 (s, 9H). GCMS peak at 304.

[00115] **Synthesis of $\text{Cp}(\text{C}_6\text{F}_5)\text{TiCl}_3$**

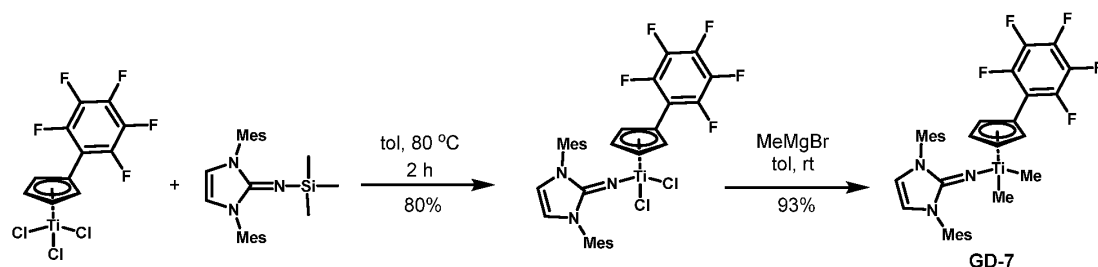


[00116] In a N_2 -filled glove box, $(\text{TMS})\text{Cp}(\text{C}_6\text{F}_5)$ (800 mg, 2.6 mmol, 0.83 equivalents) was added to titanium tetrachloride (600 mg, 3.16 mmol, 1 equivalents) dropwise and the solution was heated to 60°C. for 3 h. Upon addition of the fluorinated TMS Cp to TiCl_4 changed the color of the solution from faint yellow to dark orange. The reaction mixture was cooled down to room

temperature. Hexanes (3 mL) was added to the reaction mixture. A bright orange precipitate formation was observed. The precipitate was filtered through a fritted funnel and the residue was washed with 10 mL hexanes twice. The residue was drier under vacuum to afford orange solid (530 mg, 52%).

[00117] ^1H NMR (500 MHz, C_6D_6) δ 6.66 (tt, $J = 2.8, 1.3$ Hz, 2H), 6.07 (t, $J = 2.9$ Hz, 2H). ^{19}F NMR (471 MHz, C_6D_6) δ -138.04 (dt, $J = 20.6, 5.6$ Hz), -150.71 – -151.20 (m), -160.89 – -161.35 (m). ^{13}C NMR (126 MHz, C_6D_6) δ 145.96 – 143.95 (m), 142.99 – 140.41 (m), 139.33 – 136.89 (m), 125.12 (q, $J = 2.6$ Hz), 122.98 (s), 122.20 (t, $J = 7.2$ Hz), 108.56 (td, $J = 13.2, 4.3$ Hz).

[00118] Synthesis of GD-7:



[00119] In a N_2 -filled glovebox, the ligand 1,3-dimesityl-*N*-(trimethylsilyl)-1,3-dihydro-2H-imidazol-2-imine (163 mg, 0.42 mmol, 1 equivalents) was dissolved in 3 mL of toluene to give a clear colorless solution. The Ti-trichloride precursor (160 mg, 0.42 mmol, 1 equivalents) was dissolved in 5 mL Toluene. The ligand solution was added to the titanium trichloride precursor dropwise and heated for 16h at 60 °C to afford a homogeneous orange solution. After 16h of stirring at 60 °C, the reaction mixture was cooled down to ambient temperature. Toluene was removed under vacuum to afford an orange solid. The orange solid was filtered and washed with hexanes (2x5mL). The solid was dried under vacuum to yield the Ti- Cl_2 complex as orange crystals (224 mg, 80%).

[00120] ^1H NMR (500 MHz, C_6D_6) δ 6.80 (s, 4H), 6.51 (t, $J = 2.5$ Hz, 2H), 5.90 (t, $J = 2.9$ Hz, 2H), 5.40 (s, 2H), 2.15 (s, 12H), 2.10 (s, 6H). ^{19}F NMR (471 MHz, C_6D_6) δ -139.53 (d, $J = 20.5$ Hz), -157.67 (t, $J = 21.7$ Hz), -164.10 (t, $J = 22.7$ Hz).

[00121] In a N_2 -filled glovebox, a 20 mL vial was charged with the Ti- Cl_2 complex (120 mg, 0.18 mmol, 1 equiv), 5 mL of toluene, and a magnetic stir bar. To the solution, 3(M) MeMgBr in hexanes (0.143 mL, 0.43 mmol, 2.4 equiv) was added and the reaction mixture was stirred for 30 min at ambient temperature. The color of the reaction changes from orange to dark yellow upon addition of MeMgBr. The solution was filtered through a fritted funnel and a yellow filtrate was

obtained. The filtrate was evaporated the under vacuum to obtain a yellow solid. To the yellow solid, 2 mL of toluene was added to dissolve the solid followed by addition of 10 mL of hexanes. The slurry was filtered through a fritted funnel to obtain a yellow filtrate. The solvent was removed to afford GD-7 as a yellow solid (105 mg, 93%).

[00122] ^1H NMR (500 MHz, C_6D_6) δ 6.79 (s, 4H), 6.42 (q, $J = 2.5$ Hz, 2H), 5.60 (d, $J = 2.0$ Hz, 2H), 5.52 (t, $J = 2.8$ Hz, 2H), 2.19 (s, 12H), 2.10 (s, 6H), 0.14 (s, 6H). ^{19}F NMR (471 MHz, C_6D_6) δ -140.57 (d, $J = 22.6$ Hz), -160.11 (t, $J = 22.0$ Hz), -164.37 (t, $J = 24.3$ Hz).

[00123] Batch Reactor Polymerization Procedure

[00124] 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.

[00125] Polymerization Reactions

[00126] The results of the polymerization reactions of procatalysts GD-1, GD-2, or GD-3, in combination with CGC-2 are tabulated and discussed.

[00127] Polymerization conditions: 3.79L (1 Gal) batch reactor, 1250 g of Isopar-E; combined procatalyst (formulas (I) and (II)):activator = 1:1.2; activator: ([$\text{HNMe}(\text{C}_{18}\text{H}_{37})_2$][$\text{B}(\text{C}_6\text{F}_5)_4$]); an Al-containing co-catalyst was used in a given ratio of Al:total metal (combined formulas (I) and (II)), either butylated hydroxy toluene-triethylaluminum 2:1 adduct (BHT-TEA) or MMAO that is modified with n-octyl substituents such that the methyl:n-octyl ratio is approximately 6:1; reaction time 10 min. 160 °C: 60 g 1-octene; ethylene, pressure to reach 320 psi. 190 °C: 65 g 1-octene; ethylene, pressure to reach 410 psi.

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

Catalyst	Mw at 0 mmol of H ₂ (g/mol)	Mw at 10 mmol H ₂ (g/mol)	Mw at 20 mmol of H ₂ (g/mol)	Mw at 40 mmol of H ₂ (g/mol)	Mw at 80 mmol of H ₂ (g/mol)	Mw at 160 mmol of H ₂ (g/mol)
GD-1	239,509	32,940	17,102	10,503	6,015	--
GD-2	165,653	48,005	28,782	16,074	9,000	4,936
GD-3	168,211	26,532	15,811	7,815	4,911	--
CGC-3	338,100	204,400	139,900	92,580	52,230	28,410
CGC-2	132,100	94,560	72,530	50,970	34,290	19,730

Table 2 Constants for Chain Transfer to Hydrogen (cH₂) for Selected Catalysts at 160 °C

Catalyst	cH ₂
GD-1	0.766
GD-2	0.395
GD-3	0.961
CGC-3	0.027
CGC-2	0.040

[00128] As shown in Table 1, the GD catalysts are more sensitive to the introduction of hydrogen than the CGC catalysts. When 10 mmol of hydrogen gas was first added to the catalysts of GD-1, GD-2, and GD-3, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 70 wt.% and 90 wt.% compared to the resulting polymers of the GD catalysts that were not exposed to hydrogen. However, the M_w of the resulting polymers of the CGC catalysts only dropped from about 30 wt.% to 40 wt.% compared to the resulting polymers of the CGC catalysts that were not exposed to hydrogen.

[00129] Similarly, when the amount of hydrogen was increased from 10 mmol to 20 mmol, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 40 wt.% and 50 wt.%, whereas the resulting polymers of the CGC catalysts only dropped between about 20 wt.% and 35 wt.%. This suggests that the CGC catalysts are not as sensitive to the increased hydrogen as the GD catalysts.

[00130] Furthermore, when the amount of hydrogen was increased from 20 mmol to 40 mmol, the molecular weight, M_w , of the resulting polymers of the GD catalysts dropped between about 35 wt.% and 50 wt.%, whereas the resulting polymers of the CGC catalysts only dropped between

about 25 wt.% and 35 wt.%. Again, this suggests that the CGC catalysts are not as sensitive to the increased hydrogen as the GD catalysts.

Table 3: Polymer Composition Produced by GD-1 and CGC-2 at 40 mmol Hydrogen Loading at 160 °C

	Catalyst(s)	Hydrogen Loading (mmol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn
C1	GD-1	5	23,602	52,340	121,791	2.22
C2	CGC-2	5	34,772	92,792	193,300	2.67
I1	GD-1/CGC-2	40	6,156	26,434	131,817	4.29

[00131] BHT-TEA used as co-catalyst at 50 ratio (Al:total metal of formulas (I) and (II))

[00132] FIG. 1 shows the GPC of the produced polymers recorded in Table 3. The comonomer incorporation is constant for C1 and C2. For example, the CGC-2 catalyst has about a 10% comonomer incorporation no matter the molecular weight fraction. Surprisingly, the comonomer incorporation increases when the molecular weight fraction is greater than 50% of the weight average molecular weight, the comonomer incorporation increases.

Table 4: Polymer Composition Produced by GD-2 and CGC-2 at three different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading (mmol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn
C3	GD-2	10	22,924	53,560	140,454	2.34
C2	CGC-2	10	22,446	76,104	193,098	3.39
I2	GD-2/CGC-2	20	13,036	33,907	102,761	2.60
I3	GD-2/CGC-2	40	8,085	22,191	136,691	2.75

[00133] MMAO used as co-catalyst at 20 ratio (Al:total metal of formulas (I) and (II))

Table 5: Polymer Composition Produced by GD-3 and CGC-2 at three different Hydrogen Loadings at 160 °C

	Catalyst(s)	Hydrogen Loading	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn
C4	GD-3	10	7,622	20,730	36,430	2.72
C2	CGC-2	10	24,455	72,958	139,254	2.98
I4	GD-3/CGC-2	10	12,648	50,977	119,913	4.03
I5	GD-3/CGC-2	20	11,405	46,630	102,382	4.09
I6	GD-3/CGC-2	40	9,194	37,177	74,926	4.04

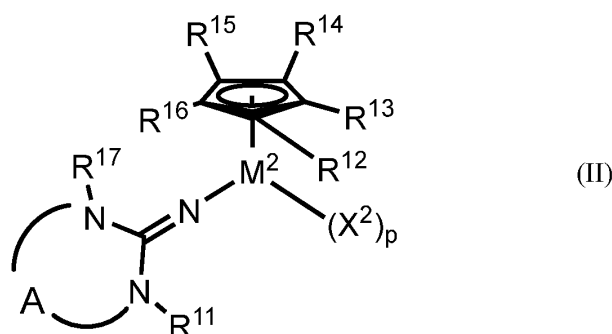
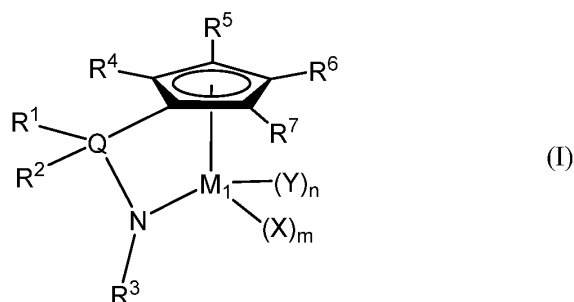
[00134] MMAO used as co-catalyst at 20 ratio (Al:total metal of formulas (I) and (II))

[00135] FIG. 2, similar to FIG. 1, shows the GPC of the produced polymers recorded in Table 4. The comonomer incorporation is constant for C3 and C2. For example, the CGC-2 catalyst has about a 10% to 15% comonomer incorporation at 10 mmol H₂ at approximately 10% molecular weight fraction to about 80% molecular weight fraction. Surprisingly, the comonomer incorporation increases when the molecular weight fraction is greater than 60% of the weight average molecular weight, the comonomer incorporation increases.

[00136] In FIG. 3, the comonomer incorporation for the polymer of I6 increases as the molecular weight increases. In contrast the polymers produced in the comparative examples, the comonomer incorporation remains constant as the molecular weight increase.

CLAIMS

1. A process of polymerizing olefin monomers to produce polyolefin, the process comprising reacting ethylene and optionally one or more olefin monomers in one or multiple reactors in the presence of a catalyst system; the catalyst system comprises two or more catalysts, at least one of which is derived from constrained geometry procatalyst according to formula (I) and at least one of which is derived from guanidine procatalyst according to formula (II):



where:

M_1 is titanium, zirconium, hafnium, or scandium;

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

(C₁–C₃₀)hydrocarbyl, or (C₁–C₃₀)heterohydrocarbyl, and each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^Y is –H, (C₁–C₃₀)hydrocarbyl, or halogen atom, wherein two X ligands can be connected to form a ring;

each Y is independently Lewis Base; optionally, X and Y can be linked to form a ring; m is 1 or 2;

n is 0, 1, or 2;

p is 1, or 2

the metal–ligand complex is overall charge-neutral;

N is nitrogen;

Q is carbon, silicon, or germanium;

R¹ and R² are independently selected from –H, (C₁–C₄₀)hydrocarbyl, and

(C₁–C₄₀)heterohydrocarbyl;

R³ are independently selected from (C₁–C₄₀)hydrocarbyl, and

(C₁–C₄₀)heterohydrocarbyl;

R⁴, R⁵, R⁶, and R⁷ are independently (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl

wherein any of the R⁴, R⁵, R⁶, and R⁷ optionally are connected to form a ring structure;

M² is titanium, zirconium, or hafnium;

each X² is independently selected from (C₁–C₅₀)hydrocarbyl,

(C₁–C₅₀)heterohydrocarbyl, –CH₂Si(R^C)_{3–J}(OR^C)_J,

–Si(R^C)_{3–J}(OR^C)_Q, –OSi(R^C)_{3–J}(OR^C)_J, –CH₂Ge(R^C)_{3–J}(OR^C)_J, –Ge(R^C)_{3–J}(OR^C)_J,

–P(R^C)_{2–K}(OR^C)_K, –P(O)(R^C)_{2–K}(OR^C)_K, –N(R^C)₂, –NH(R^C), –N(Si(R^C)₃)₂,

–NR^CSi(R^C)₃, –NHSi(R^C)₃, –OR^C, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, –S(O)R^C,

–S(O)₂R^C, –OS(O)₂R^C, –N=C(R^C)₂, –N=CH(R^C), –N=CH₂, –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)NH₂, 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 (C₁–C₃₀)hydrocarbyl, or

(C₁–C₃₀)heterohydrocarbyl, and each J is 0, 1, 2 or 3, and each K is 0, 1, or 2;

each R^Y is –H, (C₁–C₃₀)hydrocarbyl, or halogen atom, wherein two X² ligands can be connected to form a ring;

A is –C(R⁸)C(R⁹)–, –CH(R⁸)CH(R⁹)–, or –CH(R⁸)CH(R⁹)CH(R¹⁰)–, and optionally:

R^{17} and R^8 may be connected to form an aromatic or non-aromatic ring; or
 R^8 and R^9 may be connected to form an aromatic or non-aromatic ring; or
 when A is $-C(R^8)C(R^9)C(R^{10})-$, R^9 and R^{10} may be connected to form an
 aromatic or non-aromatic ring, or R^{10} and R^{11} may be connected to form
 an aromatic or non-aromatic ring; or
 when A is $-C(R^8)C(R^9)-$, R^9 and R^{11} may be connected to form an
 aromatic or non-aromatic ring;

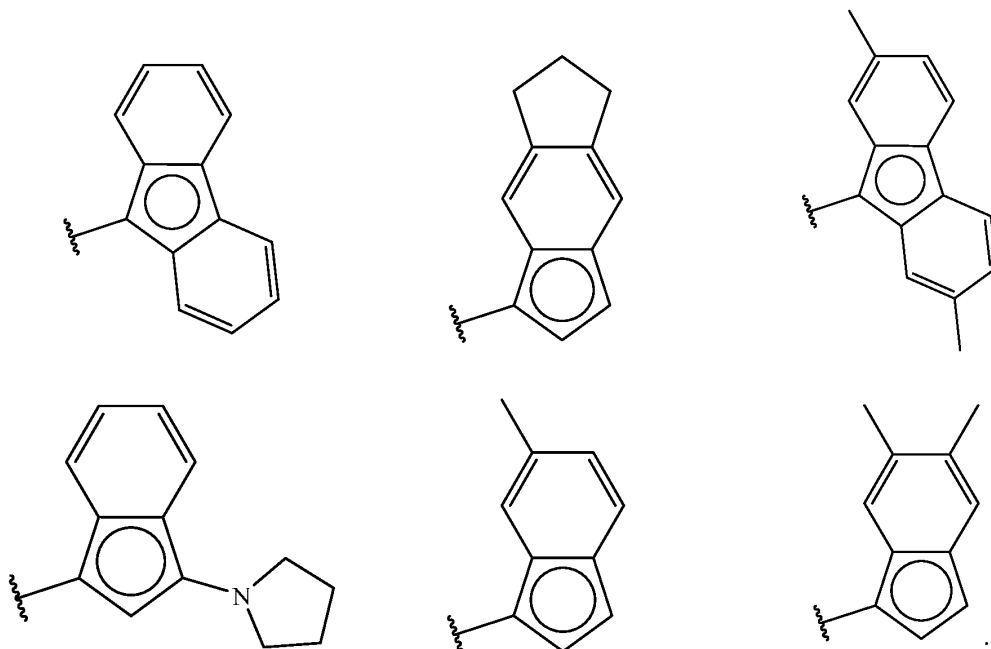
R^8 , R^9 , R^{10} , R^{11} , and R^{17} are independently (C_1-C_{50}) hydrocarbyl,

(C_1-C_{50}) heterohydrocarbyl, (C_6-C_{30}) aryl, (C_5-C_{30}) heteroaryl; and

R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} are each independently (C_1-C_{12}) alkyl, halogen substituted
 (C_1-C_{12}) alkyl, halogen substituted (C_6-C_{18}) aryl, halogen substituted (C_3-C_{50})
 cycloalkyl, or $-H$.

2. The polymerization process according to claim 1, wherein the polymerization process occurs in the presence of hydrogen feed.
3. The polymerization process according to claim 1, wherein the polymerization process occurs in the absence of hydrogen feed.
4. The polymerization process according to claim 1, wherein R^1 and R^2 are methyl, ethyl, propyl, isopropyl, isobutyl or phenyl.
5. The polymerization process according to any one of the preceding claims, wherein R^3 is independently (C_1-C_{12}) alkyl.
6. The polymerization process according to any one of the preceding claims, wherein R^4 , R^5 , R^6 , and R^7 are methyl; or R^4 and R^7 are methyl, or R^5 and R^6 are methyl or R^6 and R^7 are methyl.
7. The polymerization process according to any one of the preceding claims, wherein R^6 is $-OMe$; or R^5 is $-NMe_2$.
8. The polymerization process according to any one of claims 1 to 4, wherein:
 - (A) R^4 and R^5 are connected and form a ring optionally substituted by one or more R^S
 wherein R^S is selected from the group consisting of (C_1-C_{30}) hydrocarbyl; or
 - (B) R^6 and R^7 are connect and form ring optionally substituted by one or more R^S
 wherein R^S is selected from the group consisting of (C_1-C_{30}) hydrocarbyl; or
 - (C) both (A) and (B);

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



9. The polymerization process according to any one of the preceding claims, wherein A is $-\text{C}(\text{R}^8)\text{C}(\text{R}^9)-$ or $-\text{C}(\text{R}^8)\text{C}(\text{R}^9)\text{C}(\text{R}^{10})-$.
10. The polymerization process according to any one of the preceding claims, wherein R^8 and R^9 are $(\text{C}_1-\text{C}_{20})$ alkyl or $-\text{H}$, and R^{11} and R^{17} are substituted $(\text{C}_6-\text{C}_{18})$ aryl.
11. The polymerization process according to any one of the preceding claims, wherein R^8 , R^9 , and R^{10} are independently selected independently selected from the group consisting of: methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, methoxy, dimethylamino, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.
12. The polymerization process according to any one of the preceding claims, wherein the polymerization process is a solution polymerization reaction.
13. An ethylene-based polymer produced from the polymerization process of any preceding claim.
14. The ethylene-based polymer of claim 12, wherein the ethylene-based polymer is a bimodal polymer.