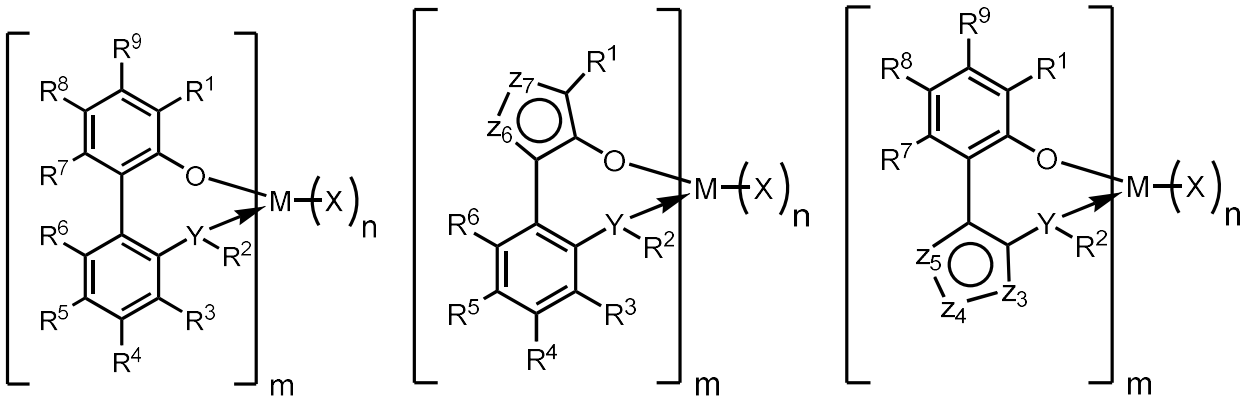
halogen, or –H, in which any two R^B groups bonded to neighboring atoms are optionally linked; Each R^7, R^8, and R^9 of B is independently chosen from (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, –Si(R^C)$_3$, –Ge(R^C)$_3$, –P(R^P)$_2$, –N(R^N)$_2$, –OR^C, –SR^C, –NO_2, –CN, –CF_3, R^CS(O)–, R^CS(O)$_2$–, (R^C)$_2$C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)$_2$NC(O)–, halogen, or –H. In formula (I), each R^C, R^N, and R^P in formula (I) is independently a (C_1−C_{50})hydrocarbyl.

[0010a] In one aspect, this present disclosure relates to a process of polymerizing olefins, the process comprising contacting ethylene, a (C_3−C_{40})alpha-olefin comonomer, and a solvent in the presence of a chain transfer agent, wherein the chain transfer agent comprises a metal that is Al, B, or Ga being in a formal oxidation state of +3, or a metal that is Zn or Mg being in a formal state of +2, and a catalyst system, the catalyst system comprising a metal–ligand complex according to formula (Ia), formula (Ib), or formula (Ic):



Ia Ib Ic

where 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 independently chosen from (C_6–C_{50})aryl, (C_6–C_{50})heteroaryl, (C_4–C_{12})diene, and halogen; n is 1 or 2; m is 2; the metal–ligand complex has 6 or fewer metal–ligand bonds; each Y is oxygen; each R^1 is carbazolyl; each R^2 is methyl; z_3, z_4, and z_5 are selected from the group consisting of sulfur, oxygen, –N(R^A)–, and −C(R^A)−, provided that exactly one of z_3, z_4, or z_5 is −C(R^A)− or that exactly two of z_3, z_4, or z_5 are −C(R^A)−; and R^3, R^4, R^5, and R^6 are independently chosen from

(C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, halogen, or –H; $z_6$and z_7 are selected from the group consisting of sulfur, oxygen, −N(R^B)−, and −C(R^B)−, provided that z_6 and z_7 are not both −C(R^B)−; and R^7, R^8, and R^9 are independently chosen from (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, –Si(R^C)$_3$, –Ge(R^C)$_3$, –P(R^P)$_2$, –N(R^N)$_2$, –OR^C, –SR^C, –NO_2, –CN, –CF_3, R^CS(O)–, R^CS(O)$_2$–, (R^C)$_2$C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)$_2$NC(O)–, halogen, or –H; each R^A is independently chosen from (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, –Si(R^C)$_3$, –Ge(R^C)$_3$, –P(R^P)$_2$, –N(R^N)$_2$, –OR^C, –SR^C, –NO_2, –CN, –CF_3, R^CS(O)–, R^CS(O)$_2$–, (R^C)$_2$C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)$_2$NC(O)–, halogen, or –H, wherein any two R^A groups bonded to neighboring atoms are optionally linked; each R^B is independently chosen from (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, –Si(R^C)$_3$, –Ge(R^C)$_3$, –P(R^P)$_2$, –N(R^N)$_2$, –OR^C, –SR^C, –NO_2, –CN, –CF_3, R^CS(O)–, R^CS(O)$_2$–, (R^C)$_2$C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)$_2$NC(O)–, halogen, or –H, wherein any two R^B groups bonded to neighboring atoms are optionally linked; and each R^C, R^N, and R^P is independently a (C_1−C_{50})hydrocarbyl.

DETAILED DESCRIPTION

[0011] 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.

[0012] Common abbreviations are listed below:

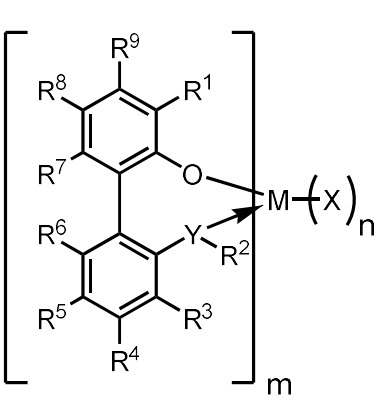
[0013] **R^C, R^Z, R^1, R^2, R^3, R^4, Z_1, Z_2, Z_3, X, Y, Q, and W**: as defined above; **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn**: benzyl; ***i*-Pr** : *iso*-propyl; ***t*-Bu** : *tert*-butyl; ***t*-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **THF** : tetrahydrofuran; **Et_2O** : diethyl ether; **CH_2Cl_2** : dichloromethane; **EtOAc** : ethyl acetate; **C_6D_6 :** deuterated benzene or benzene-*d*6 : **$CDCl_3$** : deuterated chloroform; **Na_2SO_4** : sodium sulfate; **$MgSO_4$** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi:** butyllithium; ***t*-BuLi** : *tert*-butyllithium; **K_2CO_3:** potassium carbonate; **N_2** : nitrogen gas; **PhMe**: toluene; **PPR** : parallel pressure 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; $\mathbf{R_f}$; retention fraction; **TLC** ; thin-layer chromatography; **rpm:** revolutions per minute.

[0014] The term "independently selected" followed by multiple options is used herein to indicate that individual groups appearing before the term, such as R^1, R^2, R^3, R^4, and R^C, can be identical or different, without dependency on the identity of any other group also appearing before the term.

CLAIMS

1. A process of polymerizing olefins, the process comprising contacting ethylene, a (C_3–C_{40})alpha-olefin comonomer, and a solvent in the presence of a chain transfer agent, wherein the chain transfer agent comprises a metal that is Al, B, or Ga being in a formal oxidation state of +3, or a metal that is Zn or Mg being in a formal state of +2, and a catalyst system, the catalyst system comprising a metal–ligand complex according to formula (Ia), formula (Ib), or formula (Ic):



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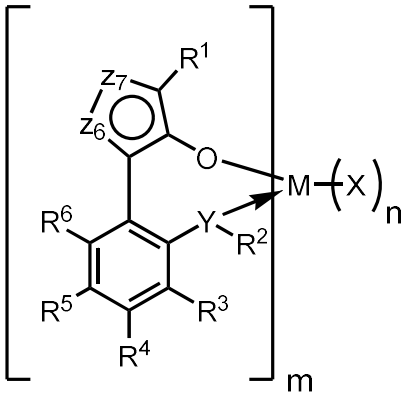

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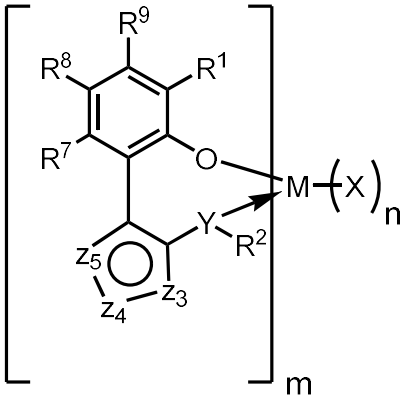


Ic

where

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 independently chosen from (C_6–C_{50})aryl, (C_6–C_{50})heteroaryl, (C_4–C_{12})diene, and halogen;

n is 1 or 2;

m is 2;

the metal–ligand complex has 6 or fewer metal–ligand bonds;

each Y is oxygen;

each R^1 is carbazolyl;

each R^2 is methyl;

z_3, z_4, and z_5 are selected from the group consisting of sulfur, oxygen, $-N(R^A)-$, and $-C(R^A)-$, provided that exactly one of z_3, z_4, or z_5 is $-C(R^A)-$ or that exactly two of z_3, z_4, or z_5 are $-C(R^A)-$; and

R^3, R^4, R^5, and R^6 are independently chosen from $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, halogen, or –H;

$z_6$and z_7 are selected from the group consisting of sulfur, oxygen, $–N(R^B)–$, and $–C(R^B)–$, provided that z_6 and z_7 are not both $–C(R^B)–$; and

R^7, R^8, and R^9 are independently chosen from $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $–Si(R^C)_3$, $–Ge(R^C)_3$, $–P(R^P)_2$, $–N(R^N)_2$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, halogen, or –H;

each R^A is independently chosen from $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $–Si(R^C)_3$, $–Ge(R^C)_3$, $–P(R^P)_2$, $–N(R^N)_2$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, halogen, or –H, wherein any two R^A groups bonded to neighboring atoms are optionally linked;

each R^B is independently chosen from $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $–Si(R^C)_3$, $–Ge(R^C)_3$, $–P(R^P)_2$, $–N(R^N)_2$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, halogen, or –H, wherein any two R^B groups bonded to neighboring atoms are optionally linked; and

each R^C, R^N, and R^P is independently a $(C_1–C_{50})$hydrocarbyl.

2. The polymerization process according to claim 1, wherein the metal-ligand complex has a structure according to formula (Ib), and wherein z_6 is sulfur and z_7 is –C(H)–, or z_6 is –C(H)– and z_7 is sulfur .

3. The polymerization process according to claim 1 or 2, wherein the metal-ligand complex has a structure according to formula (Ia) or formula (Ib), and wherein R^3, R^4, R^5 and R^6 are $–C(H)–$.

4. The polymerization process according to claim 1 or 3, wherein the metal-ligand complex has a structure according to formula (Ia) or formula (Ic), and wherein R^7, R^8, and R^9 are −C(H)−.

5. The polymerization process according to claim 1 or 3, wherein the metal-ligand complex has a structure according to formula (Ia) or formula (Ic), and wherein R^7 and R^9 are −C(H)−, and R^8 is (C_1-C_{20})alkyl.

6. The polymerization process of any one of claims 1 to 5, wherein the chain transfer agent is dialkyl zinc or trialkyl aluminum.

7. The polymerization process according to any one of claims 1 to 6, wherein the polymerization process occurs in a reactor.

8. The polymerization process according to any one of claims 1 to 7, wherein the polymerization process occurs at a reaction temperature from 120 °C to 190 °C.

9. The polymerization process according to any one of claims 1 to 8, wherein the catalyst system further comprises a co-catalyst.

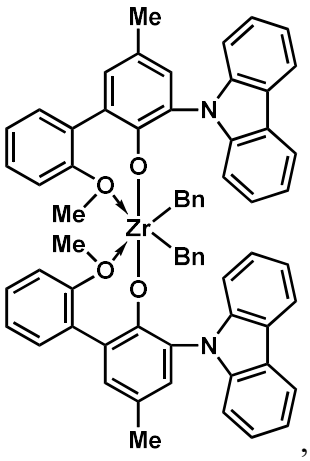
10. The polymerization process according to any one of claims 1 to 9, wherein the chain transfer agent is diethyl zinc, trimethyl aluminum, triethyl aluminum, or trioctyl aluminum.

11. The polymerization process according to any one of claims 1 to 5 or 7 to 9, wherein the chain transfer agent comprises a metal that is Zn or Mg being in a formal state of +2.

12. The polymerization process according to any one of claims 1 to 9 or 11, wherein the chain transfer agent is dialkyl zinc.

13. The polymerization process according to any one of claims 1 to 12, wherein each X is independently benzyl, phenyl, or chloro.

14. The polymerization process according to any one of claims 1 or 6 to 11, wherein the metal-ligand complex is one of the following structures: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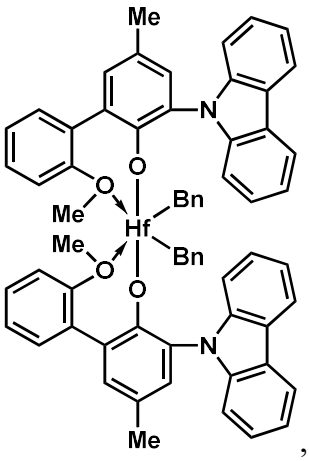
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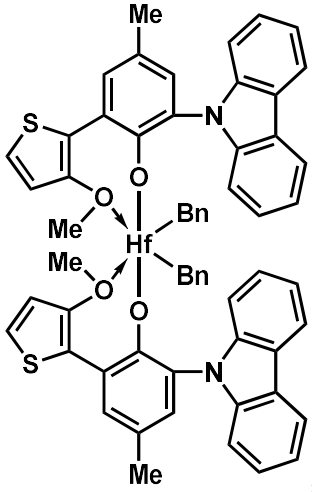
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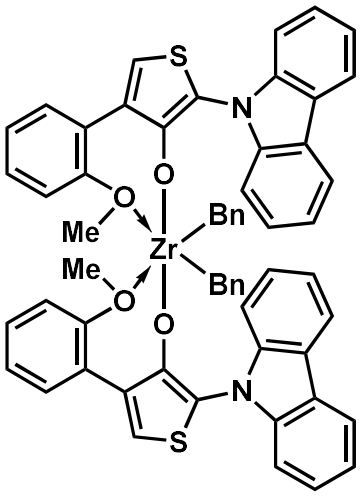
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