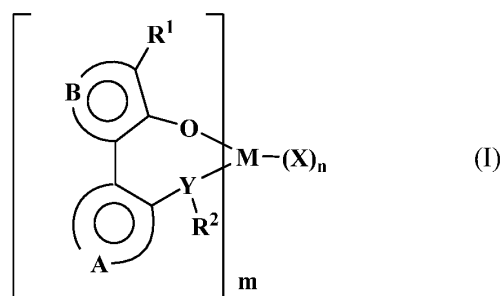


CLAIMS

1. A process of polymerizing olefins, the process comprising contacting ethylene, a (C₃–C₄₀)alpha-olefin comonomer, and a solvent in the presence of a chain transfer agent and a catalyst system, the catalyst system comprising a metal–ligand complex according to formula (I):



where

M is a metal chosen from titanium, 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 unsaturated

(C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon,

(C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, cyclopentadienyl,

substituted cyclopentadienyl, (C₄–C₁₂)diene, halogen, –N(R^N)₂, and –NCOR^C;

n is 1, 2, or 3;

m is 1 or 2;

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

each Y is independently selected from oxygen or sulfur;

each R¹ is independently selected from the group consisting of (C₁–C₅₀)hydrocarbyl,

(C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃,

–Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–,

–P(O)(R^P)₂, 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, and –H;

each R² is independently chosen from (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl,

(C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, and –Ge(R^C)₃;

each A is independently chosen from $-z_3-z_4-z_5-$ or $-C(R^3)C(R^4)C(R^5)C(R^6)-$, where:

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 $-H$;

each B is independently chosen from $-z_6-z_7-$ or $-C(R^7)C(R^8)C(R^9)-$, where:

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, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^C S(O)-$, $R^C S(O)_2-$, $(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2NC(O)-$, 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, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^C S(O)-$, $R^C S(O)_2-$, $(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2NC(O)-$, 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, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^C S(O)-$, $R^C S(O)_2-$, $(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2NC(O)-$, 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 in formula (I) is independently a (C_1-C_{50}) hydrocarbyl;

2. The catalyst system according to claim 1, wherein:

M is zirconium or hafnium;

each X is independently chosen from (C₆–C₂₀)aryl, (C₄–C₂₀)heteroaryl, (C₄–C₁₂)diene, or a halogen;

each Y is oxygen; and

each R¹ is independently chosen from (C₁–C₅₀)aryl or (C₄–C₅₀)heteroaryl.

3. The polymerization process according to claim 1 or 2, wherein each B is –S–C(H)– or –C(H)–S–.

4. The polymerization process according to claim 1 or claim 2, wherein each A is –C(H)C(H)C(H)C(H)–.

5. The polymerization process according to any one of claims 1-4, wherein each R¹ is carbazolyl or substituted carbazolyl and each R² is methyl.

6. The polymerization process according to any one of claims 1-4, wherein each R¹ is phenyl or a substituted phenyl.

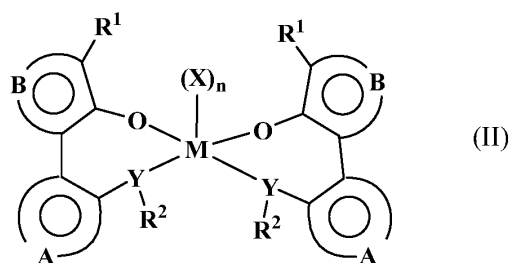
7. The polymerization process according to any one of claims 1-4, wherein each R¹ is a substituted phenyl chosen from 2,4,6-trimethylphenyl; 2,4,6-tri(*iso*-propyl)phenyl; 3,5-di-*tert*-butylphenyl, or 3,5-diphenylphenyl.

8. The polymerization process according to any one of claims 1-7, wherein each B is –C(H)C(H)C(H)–.

9. The polymerization process according to any one of claims 1-7, wherein each B is –C(H)C(R⁸)C(H)–, where R⁸ is (C₁–C₂₀)alkyl.

10. The polymerization process according to any one of claims 1 or 3 to 9, wherein Y is sulfur.

11. The polymerization process according to claim 1, wherein m is 2 and the metal-ligand complex has a structure according to formula (II):



where R^1 , R^2 , A, B, Y, and X are as defined in formula (I); and n is 1 or 2.

12. The polymerization process according to claim 11, wherein:
M is zirconium or hafnium;
each X is independently chosen from (C_6-C_{50}) aryl, (C_6-C_{50}) heteroaryl, (C_4-C_{12}) diene, or halogen;
each Y is oxygen;
each R^1 and R^2 is independently chosen from (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, halogen, and hydrogen.
13. The polymerization process according to claim 11 or 12, wherein each B is $-S-C(H)-$ or $-C(H)-S-$.
14. The polymerization process according to any one of claims 11-13, wherein each R^1 is carbazolyl and each R^2 is methyl.
15. The polymerization process according to any one of claims 11-13, wherein each R^1 is independently 3,6-di-*tert*-butylcarbazol-9-yl or 2,7-di-*tert*-butylcarbazol-9-yl.
16. The polymerization process according to any one of claims 11-13, wherein each R^1 is 3,5-di-*tert*-butylphenyl.
17. The polymerization process according to any one of claims 11-13, wherein each R^1 is 2,4,6-trimethylphenyl.

18. The polymerization process according to any one of claims 11-17, wherein each B is $-C(R^7)C(R^8)C(R^9)-$, where R^7 , R^8 , and R^9 are $-H$.
19. The polymerization process according to any one of claims 11-17, wherein each B is $-C(R^7)C(R^8)C(R^9)-$, where R^7 and R^9 are $-H$, and R^8 is (C_1-C_{20}) alkyl.
20. The polymerization process of any one of claims 1 to 19, wherein the polymerization process occurs in a reactor.
21. The polymerization process according to 1 to 20, wherein the polymerization process occurs at a reaction temperature from 120 °C to 190 °C.
22. The polymerization process of any one of claims 1 to 21, wherein the chain transfer agent is dialkyl zinc or trialkyl aluminum.
23. The polymerization process of any one of claims 1 to 22, wherein the catalyst system further comprises a co-catalyst.
24. The polymerization process of any one of claims 1 to 23, wherein the chain transfer agent is diethyl zinc, trimethyl aluminum, triethyl aluminum, or trioctyl aluminum.