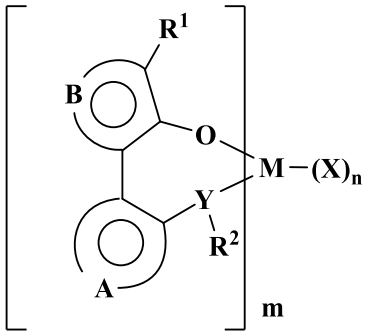
CLAIMS

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 and a catalyst system, the catalyst system comprising a metal–ligand complex according to formula (I):



(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 (C_2–C_{50})hydrocarbon, unsaturated (C_2–C_{50})heterohydrocarbon, (C_1–C_{50})hydrocarbyl, (C_6–C_{50})aryl, (C_6–C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4–C_{12})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 R^1 is independently selected from the group consisting of (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, $R^CS(O)$–, –$P(O)(R^P)_2$, $R^CS(O)_2$–, $(R^C)_2C{=}N$–, $R^CC(O)O$–, $R^COC(O)$–, $R^CC(O)N(R)$–, $(R^C)_2NC(O)$–, halogen, and −H;

each 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, –$Si(R^C)_3$, 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, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, 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 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 (C_6-C_{20})aryl, (C_4-C_{20})heteroaryl, (C_4-C_{12})diene, or a halogen;

each Y is oxygen; and

each R^1 is independently chosen from (C_1–C_{50})aryl or (C_4–C_{50})heteroaryl.

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

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

5. The polymerization process according to claim 1, wherein each R^1 is carbazolyl or substituted carbazolyl and each R^2 is methyl.

6. The polymerization process according to claim 1, wherein each R^1 is phenyl or a substituted phenyl.

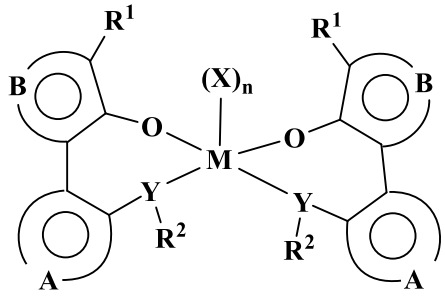
7. The polymerization process according to claim 1, wherein each R^1 is a substituted phenyl chosen from 2,4,6-trimethylphenyl; 2,4,6-tri(*iso*-propyl)phenyl; 3,5-di-*tert*-butylphenyl, or 3,5-diphenylphenyl.

8. The polymerization process according to claim 1, wherein each B is −C(H)C(H)C(H)−.

9. The polymerization process according to claim 1, wherein each B is −C(H)C(R^8)C(H)−, where R^8 is (C_1–C_{20})alkyl.

10. The polymerization process according to claim 1, 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):



(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, wherein each B is −S−C(H)− or −C(H)−S−.

14. The polymerization process according to claim 11, wherein each R^1 is carbazolyl and each R^2 is methyl.

15. The polymerization process according to claim 11, 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 claim 11, wherein each R^1 is 3,5-di-*tert*-butylphenyl.

17. The polymerization process according to claim 11, wherein each R^1 is 2,4,6-trimethylphenyl.

18. The polymerization process according to claim 11, 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 claim 11, 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 chain transfer agent is dialkyl zinc or trialkyl aluminum.