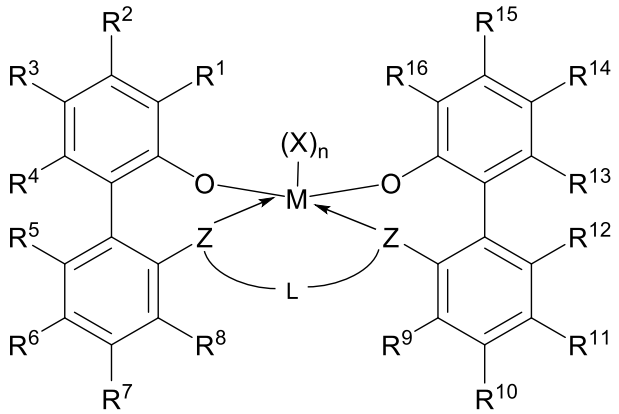
CLAIMS

1. A process of polymerizing olefin monomers, the process comprising reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system, wherein the catalyst system comprises: an activator; hydrocarbyl-modified methylaluminoxane having less than 25 mole percent trialkyl aluminum based on the total moles of aluminum, wherein trialkyl aluminum has a formula of $AlR^{A1}R^{B1}R^{C1}$, where R^{A1}, R^{B1}, and R^{C1} are independently linear (C_1−C_{40})alkyl, branched (C_1−C_{40})alkyl, or (C_1−C_{40})aryl; and one or more metal-ligand complexes comprising a metal–ligand complex according to formula (I):



(I)

where:

M is titanium, zirconium, hafnium, scandium, yttrium, or an element of the lanthanide series of the periodic table;

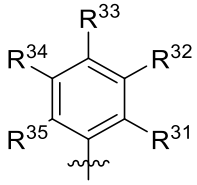
n is 1, 2, or 3;

each X is a monodentate 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 $-N(R^N)COR^C$, optionally, two X may be linked together;

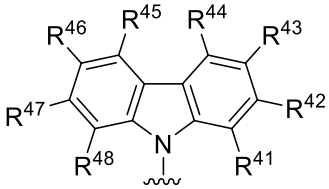
the metal–ligand complex is overall charge-neutral;

each Z is independently chosen from −O−, −S−, $-N(R^N)-$, or $-P(R^P)-$;

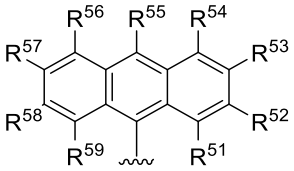
R^1 and R^{16} are independently selected from the group consisting of –H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, −CN, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N{=}C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −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^N)−, (R^C)$_2$NC(O)−, or halogen;

R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, and R^{15} are independently selected from −H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −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)−, and halogen;

L is (C_1–C_{40})hydrocarbylene or (C_2–C_{40})heterohydrocarbylene; and

each R^C, R^P, and R^N in formula (I) is independently a (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl, or –H;

wherein the ratio of moles of aluminum in the hydrocarbyl-modified methylaluminoxane to moles of metal in the metal−ligand complex is from greater than 20 to greater than 300.

2. The polymerization process according to claim 1, wherein the ratio of moles of aluminum in the hydrocarbyl-modified methylaluminoxane to moles of metal in the metal−ligand complex is less than 500.

3. The polymerization process according to claim 1, where the hydrocarbyl-modified methylaluminoxane has less than 20 mole percent of trialkyl aluminum based on the total moles of aluminum.

4. The polymerization process according to claim 1, where the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent of trialkyl aluminum based on the total moles of aluminum or where the hydrocarbyl-modified methylaluminoxane has less than 10 mole percent of trialkyl aluminum based on the total moles of aluminum.

5. The polymerization process according to claim 1, where the hydrocarbyl-modified methylaluminoxane is modified methylaluminoxane.

6. The polymerization process according to claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (III).

7. The polymerization process according to claim 6, wherein R^{42} and R^{47} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$ or wherein R^{43} and R^{46} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

8. The polymerization process according to claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (II).

9. The polymerization process according to claim 8, wherein R^{32} and R^{34} are (C_1-C_{12})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

10. The polymerization process according to claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (IV).

11. The polymerization process according to claim 10, wherein at least two of R^{52}, R^{53}, R^{55}, R^{57}, and R^{58} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

12. The polymerization process according to claim 1, wherein R^8 and R^9 are independently selected from (C_1-C_{20})alkyl.

13. The polymerization process according to claim 1, wherein R^8 and R^9 are independently selected from methyl, ethyl, 1-propyl, or 2-propyl.

14. The polymerization process according to claim 1, wherein R^3 and R^{14} are (C_1-C_{10})alkyl.

15. The polymerization process according to claim 1, wherein R^7 and R^{10} are halogen.

16. The polymerization process according to claim 1, wherein R^6 and R^{11} are *tert*-butyl.

17. The polymerization process according to claim 1, wherein L is chosen from $-CH_2(CH_2)_mCH_2-$, where m is 1 to 3, $-CH_2Si(R^C)(R^D)CH_2-$, $-CH_2Ge(R^C)(R^D)CH_2-$, $-CH_2(CH_3)CH_2CH^*(CH_3)$, bis(methylene)cyclohexan-1,2-diyl; $-CH_2CH(R^C)CH_2-$, $-CH_2C(R^C)_2CH_2-$, where each R^C in L is (C_1-C_{20})hydrocarbyl and R^D in L is (C_1-C_{20})hydrocarbyl.

18. The polymerization process according to claim 1, wherein the olefin monomer is (C_3-C_{20})α-olefin.

19. The polymerization process according to claim 1, wherein the olefin monomer is cyclic olefin.

20. The polymerization process according to claim 1, wherein the olefin monomer is not (C_3–C_{20})α-olefin.