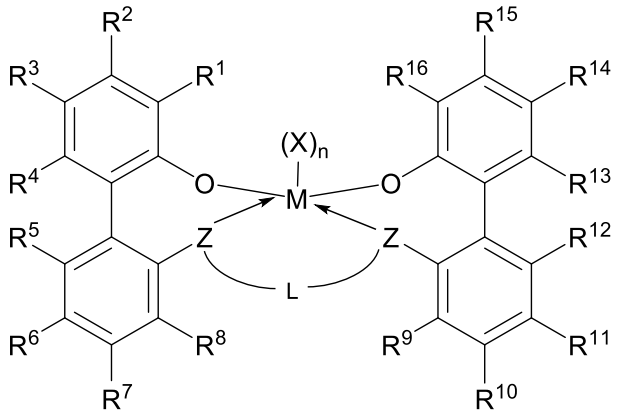
CLAIMS

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;

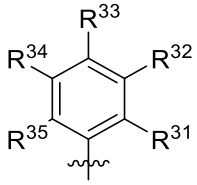
n is 1, 2, or 3;

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;

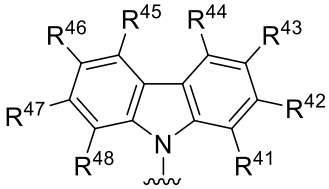
the metal–ligand complex is overall charge-neutral;

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

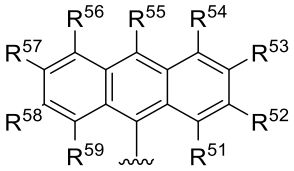
R^1 and R^{16} are independently selected from the group consisting of –H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, −CN, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N{=}C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, 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 ~~less~~from greater than ~~500.~~ 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 ~~from greater than 20 to~~ less than ~~300~~500.

3. The polymerization process according to claim 1 ~~or claim 2~~, 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 ~~or claim 2~~, where the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent of trialkyl aluminum based on the total moles of aluminum~~.~~

~~5. The polymerization process according to claim 1 or claim 2,~~ or where the hydrocarbyl-modified methylaluminoxane has less than 10 mole percent of trialkyl aluminum based on the total moles of aluminum.

~~6~~5. The polymerization process according to ~~any one of~~ claim 1 ~~to claim 5~~, where the hydrocarbyl-modified methylaluminoxane is modified methylaluminoxane.

~~7.~~6. The polymerization process according to ~~any one of claims~~ claim 1 ~~to 6, wherein R^1 and R^{16} are identical.~~

~~8. The polymerization process according to any one of the preceding claims~~, wherein at least one of R^1 and R^{16} is a radical having formula (III).

~~9~~7. The polymerization process according to claim ~~8~~6, wherein R^{42} and R^{47} are $(C_1–C_{20})$hydrocarbyl or $–Si[(C_1–C_{20})hydrocarbyl]_3$~~.~~

~~10. The polymerization process according to claim 8,~~ or wherein R^{43} and R^{46} are $(C_1–C_{20})$hydrocarbyl or $–Si[(C_1–C_{20})hydrocarbyl]_3$.

~~11~~8. The polymerization process according to ~~any one of claims~~claim 1 ~~to 6~~, wherein at least one of R^1 and R^{16} is a radical having formula (II).

~~12~~9. The polymerization process according to claim ~~11~~8, wherein R^{32} and R^{34} are $(C_1–C_{12})$hydrocarbyl or $–Si[(C_1–C_{20})hydrocarbyl]_3$.

~~13~~10. The polymerization process according to ~~any one of claims~~claim 1 ~~to 6~~, wherein at least one of R^1 and R^{16} is a radical having formula (IV).

~~14~~11. The polymerization process according to claim ~~13~~10, wherein at least two of R^{52}, R^{53}, R^{55}, R^{57}, and R^{58} are $(C_1–C_{20})$hydrocarbyl or $–Si[(C_1–C_{20})hydrocarbyl]_3$.

~~15~~12. The polymerization process according to ~~any of the preceding claims, wherein:~~

~~at least one of R^5, R^6, R^7, and R^8 is a halogen atom; and~~

~~at least one of R^9, R^{10}, R^{11}, and R^{12} is a halogen atom.~~

~~16. The polymerization process according to any one of claims~~claim 1 ~~to 14~~, wherein R^8 and R^9 are independently selected from $(C_1–C_{20})$alkyl.

~~17~~13. The polymerization process according to ~~any one of claims~~claim 1 ~~to 14~~, wherein R^8 and R^9 are independently selected from methyl, ethyl, 1-propyl, or 2-propyl.

~~18~~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 ~~any of the preceding claims~~claim 1, wherein ~~R^3~~R^7 and ~~R^{14}~~R^{10} are ~~$(C_1–C_{10})$alkyl~~halogen.

~~19~~16. The polymerization process according to ~~any one of the preceding claims, wherein R^3 and R^{14} are methyl, R^6 and R^{11} are halogen.~~

~~20. The polymerization process according to any one of claims 1-15, wherein R^7 and R^{10} are halogen.~~

~~21. The polymerization process according to any one of claims 1-15~~claim 1, wherein R^6 and R^{11} are *tert*-butyl.

~~22.~~17. The polymerization process according to ~~any one of claims~~claim 1 ~~to 15, wherein R^3 and R^{14} are *tert*-octyl or *n*-octyl.~~

~~23. The polymerization process according to any one of the preceding claims~~, 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.

~~24~~18. The polymerization process according to ~~any one of the preceding claims, wherein M is zirconium or hafnium.~~

~~25. The polymerization process according to any one of the preceding claims~~claim 1, wherein the olefin monomer is $(C_3–C_{20})$α-olefin.

~~26~~19. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein the olefin monomer is cyclic olefin.

~~27~~20. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein the olefin monomer is not $(C_3–C_{20})$α-olefin.

~~28. The polymerization process according to any one of the preceding claims, wherein the polymerization process is a solution polymerization reaction.~~