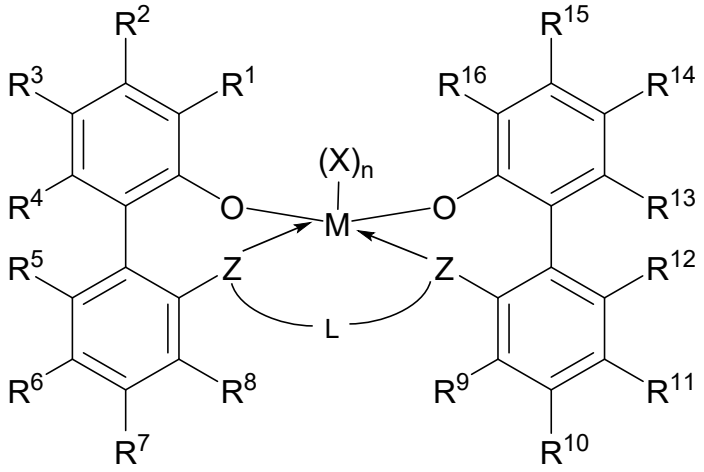
SUMMARY

[0008] There is an ongoing need to create a catalyst system while maintaining catalyst efficiency, reactivity, and the ability to produce polymers with good physical properties.

[0009] This disclosure includes processes of polymerizing olefin monomers. In one or more examples, the process includes reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system. The catalyst system includes hydrocarbyl-modified methylaluminoxane and a metal-ligand complex. The hydrocarbyl-modified methylaluminoxane having less than 25 mole percent trihydrocarbyl aluminum compound $AlR^AR^BR^C$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^A, R^B, and R^C are independently $(C_1–C_{40})$alkyl; and one or more metal–ligand complexes according to formula (I):

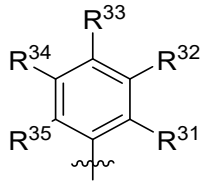


(I)

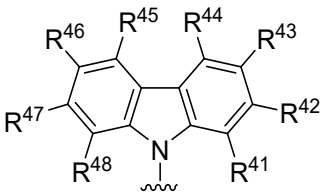
[0010] In formula (I), M is titanium, zirconium, hafnium, yttrium, or an element of the lanthanide series of the periodic table having a formal oxidation state of +2, +3, or +4. Subscript n of $(X)_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, saturated $(C_2–C_{50})$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 $–N(R^N)COR^C$. The metal–ligand complex is overall charge-neutral. Each Z is independently chosen from –O–, –S–, $–N(R^N)–$, or $–P(R^P)–$. L is $(C_1–C_{40})$hydrocarbylene or $(C_2–C_{40})$heterohydrocarbylene.

[0011] In formula (I), 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, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen.

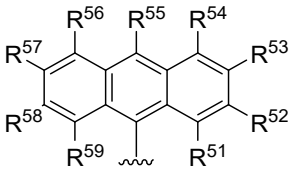
[0012] In formula (I), R^1 and R^{16} are independently selected from the group consisting of –H, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, −CN, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N=C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

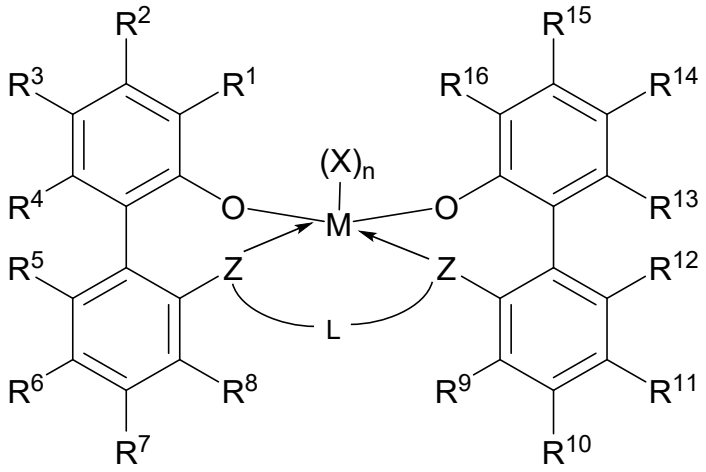
[0013] In formulas (II), (III), and (IV), each of R^{31-35}, R^{41-48}, and R^{51-59} is independently chosen from –H, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, −CN, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, or halogen.

[0014] In formulas (I), (II), (III), and (IV), each R^C, R^P, and R^N is independently a (C_1-C_{30})hydrocarbyl, (C_1-C_{30})heterohydrocarbyl, or −H.

[0014a] In one aspect, there is provided 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:

hydrocarbyl-modified methylaluminoxane having less than 20 mole percent and greater than 5 mole percent trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A1}, R^{B1}, and R^{C1} are independently linear (C_1-C_{40})alkyl, branched (C_1-C_{40})alkyl, or (C_6-C_{40})aryl; and

one or more metal–ligand complexes according to formula (I):



(I)

where:

M is titanium, zirconium, hafnium, or scandium;

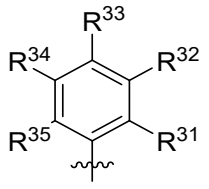
n is 1, 2, or 3;

each X is a halogen, unsubstituted (C_1-C_{20}) hydrocarbyl, unsubstituted (C_1-C_{20})hydrocarbyl, C(O)O-, or R^KR^LN, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{20})hydrocarbyl;

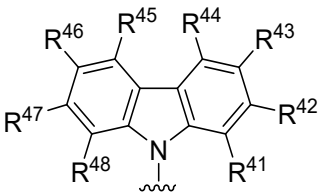
the metal–ligand complex is overall charge-neutral;

each Z is −O−;

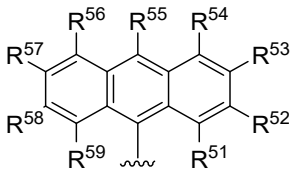
R^1 and R^{16} are independently selected from radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(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)$_3$, 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)$_3$, 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 catalyst system does not contain a borate activator; and

wherein the olefin monomer is (C_3−C_{20})α-olefin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a chart of the catalyst efficiency of bis-phenylphenoxy 4 (BPP-4) and BPP-11 as a function of MMAO.

[0016] FIG. 2 is a chart of the catalyst efficiency of BPP-2 and BPP-4 as a function of MMAO.

[0017] FIG. 3 is a chart of the catalyst efficiency of BPP-1 to BPP-6 and BPP-12 as a function of MMAO.

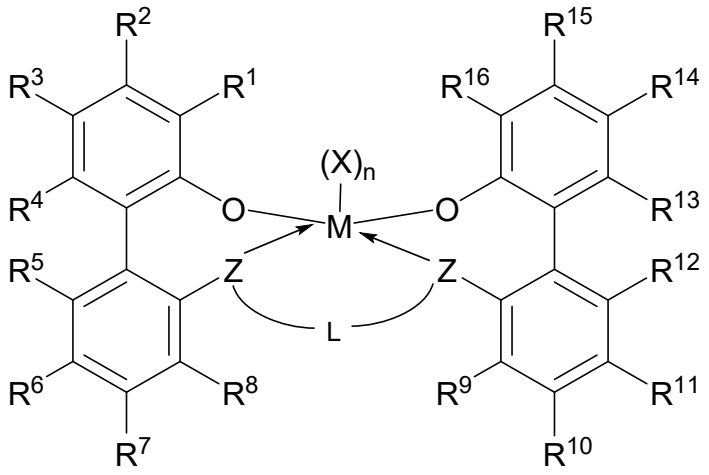
[0018] FIG. 4 is a chart of the catalyst efficiency of BPP-9 and BPP-10 as a function of MMAO.

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:

hydrocarbyl-modified methylaluminoxane having less than 20 mole percent and greater than 5 mole percent trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A1}, R^{B1}, and R^{C1} are independently linear (C_1–C_{40})alkyl, branched (C_1–C_{40})alkyl, or (C_6–C_{40})aryl; and

one or more metal–ligand complexes according to formula (I):



(I)

where:

M is titanium, zirconium, hafnium, or scandium;

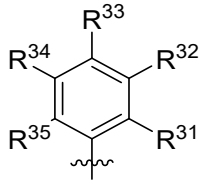
n is 1, 2, or 3;

each X is a halogen, unsubstituted (C_1-C_{20}) hydrocarbyl, unsubstituted (C_1-C_{20})hydrocarbyl, C(O)O-, or R^KR^LN, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{20})hydrocarbyl;

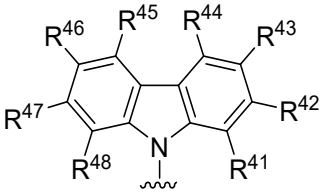
the metal–ligand complex is overall charge-neutral;

each Z is −O−;

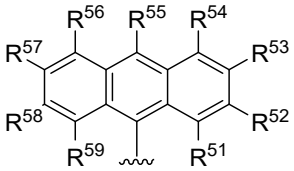
R^1 and R^{16} are independently selected from radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(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)$_3$, 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)$_3$, 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 catalyst system does not contain a borate activator; and

wherein the olefin monomer is (C_3−C_{20})α-olefin.

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

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

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

5. The polymerization process according to any one of claims 1 to 4, wherein R^1 and R^{16} are identical.

6. 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).

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

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

9. The polymerization process according to any one of claims 1 to 4, wherein at least one of R^1 and R^{16} is a radical having formula (II).

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

11. The polymerization process according to any one of claims 1 to 4, wherein at least one of R^1 and R^{16} is a radical having formula (IV).

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

13. 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.

14. The polymerization process according to any of claims 1 to 12, wherein R^8 and R^9 are independently (C_1-C_4)alkyl.

15. The polymerization process according to any of the preceding claims, wherein R^3 and R^{14} are (C_1-C_{20})alkyl.

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.

17. The polymerization process according to any one of claims 1-13, wherein R^6 and R^{11} are *tert*-butyl.

18. The polymerization process according to any one of claims 1 to 13, wherein R^3 and R^{14} are *tert*-octyl or *n*-octyl.

19. The polymerization process according to any one of the preceding claims, wherein M is Zr or Sc.

20. 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, $-CH_2Si(R^C)(R^D)CH_2-$, $-CH_2Ge(R^C)(R^D)CH_2-$, $-CH(CH_3)CH_2CH(CH_3)-$, 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.

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

22. The polymerization process according to any one of the preceding claims, wherein X is selected from methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2,2-dimethylpropyl, phenyl, benzyl, or chloro.

23. The polymerization process according to any one of the preceding claims, wherein each of R^{31-35}, R^{41-48}, and R^{51-59} is independently chosen from -H and (C_1-C_{20})hydrocarbyl.