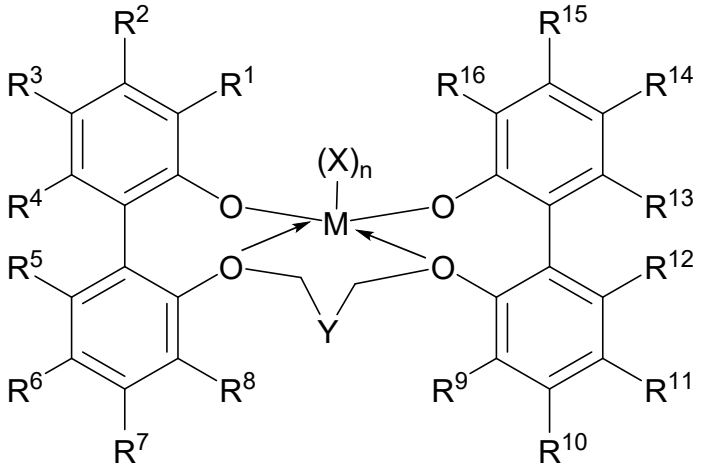
SUMMARY

[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. There is a further need to produce uniformed polymer compositions.

[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 modified-hydrocarbyl methylaluminoxane and a procatalyst. The modified-hydrocarbyl methylaluminoxane having less than 50 mole $AlR^AR^BR^C$ based on the total moles of aluminum, where R^A, R^B, and R^C 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):

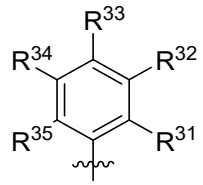


(I)

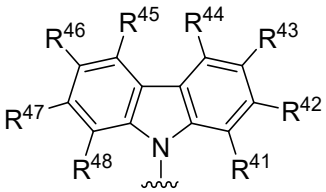
[0010] In formula (I), M is titanium, zirconium, or hafnium. Subscript n of $(X)_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, $(C_1–C_{50})$hydrocarbyl, $(C_6–C_{50})$aryl, $(C_6–C_{50})$heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(C_4–C_{12})$diene, halogen, $–N(R^N)_2$, and $–N(R^N)COR^C$; and the metal–ligand complex is overall charge-neutral.

[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.

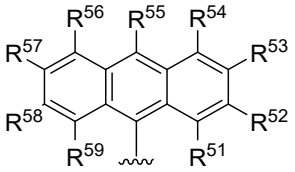
[0012] In formula (I), R^1 and R^{16} are independently selected from the group consisting of –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, R^CS(O)−, R^CS(O)$_2$−, −N=C(R^C)$_2$, R^CC(O)O−, R^COC(O)−,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

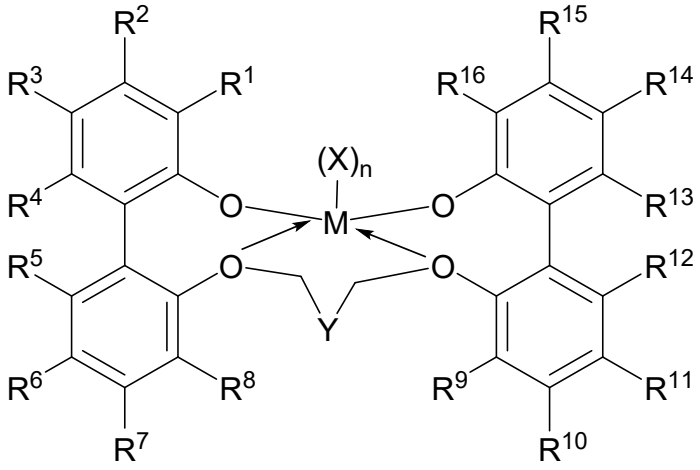
[0014] In formula (I), Y is CH_2, CHR^{21}, $CR^{21}R^{22}$, $SiR^{21}R^{22}$, or $GeR^{21}R^{22}$, where R^{21} and R^{22} are (C_1–C_{20})alkyl; provided that when Y is CH_2, at least one of R^8 and R^9 is not –H.

[0015] In formulas (I), (II), (III), and (IV), 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.

[0015a] 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 greater than 2.5 mole percent and less than 50 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A1}, R^{B1}, and R^{C1} are independently methyl, ethyl, propyl, 2-propyl, butyl, *tert*-butyl, or octyl; and

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



(I)

where:

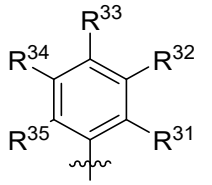
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

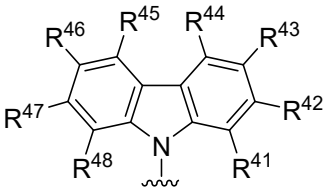
each X is a monodentate ligand independently chosen from (C_1–C_{20})hydrocarbyl, phenyl, benzyl, and halogen;

the metal–ligand complex is overall charge-neutral;

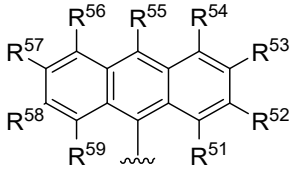
R^1 and R^{16} are independently selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from –H, (C_1–C_{20})hydrocarbyl, −Si(R^C)$_3$, Si[(C_1–C_{20})hydrocarbyl]$_3$, −OR^C, −SR^C, −CN, −CF_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)$_3$, −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;

Y is CH_2, CHR^{21}, $CR^{21}R^{22}$, $SiR^{21}R^{22}$, or $GeR^{21}R^{22}$, where R^{21} and R^{22} are (C_1–C_{20})alkyl; provided that when:

(1) Y is CH_2, then at least one of R^8 and R^9 is not –H;

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

wherein the catalysts system does not contain a borate activator.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 is a chart of the catalyst efficiency of metal-ligand complexes I1, I3, and I7 as a function of the type of MMAO co-catalyst.

DETAILED DESCRIPTION

[0017] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

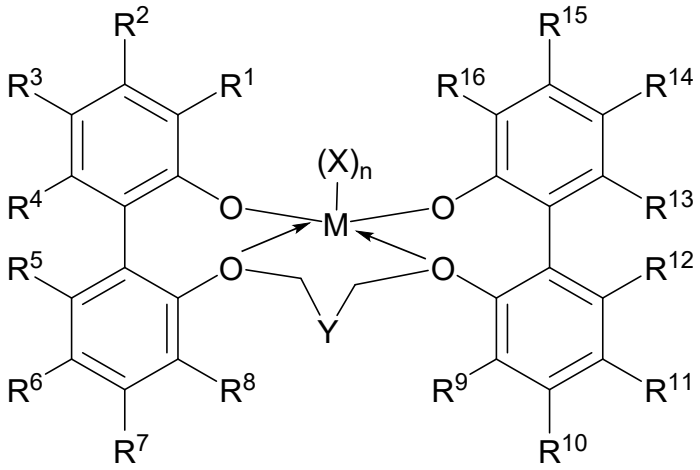
[0018] Common abbreviations are listed below:

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 greater than 2.5 mole percent and less than 50 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A1}, R^{B1}, and R^{C1} are independently methyl, ethyl, propyl, 2-propyl, butyl, *tert*-butyl, or octyl; and

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



(I)

where:

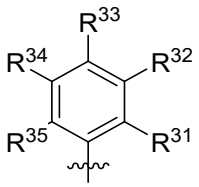
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

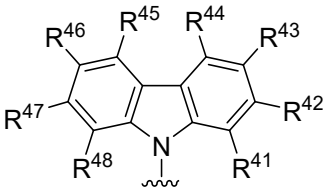
each X is a monodentate ligand independently chosen from (C_1–C_{20})hydrocarbyl, phenyl, benzyl, and halogen;

the metal–ligand complex is overall charge-neutral;

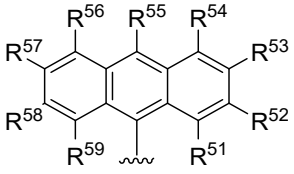
R^1 and R^{16} are independently selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from –H, $(C_1–C_{20})$hydrocarbyl, $-Si(R^C)_3$, $Si[(C_1–C_{20})hydrocarbyl]_3$, $-OR^C$, $-SR^C$, −CN, $-CF_3$, 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, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2-OR^C$, $-SR^C$, $-NO_2$, −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;

Y is CH_2, CHR^{21}, $CR^{21}R^{22}$, $SiR^{21}R^{22}$, or $GeR^{21}R^{22}$, where R^{21} and R^{22} are $(C_1–C_{20})$alkyl; provided that when:

(1) Y is CH_2, then at least one of R^8 and R^9 is not –H;

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

wherein the catalysts system does not contain a borate activator.

2. The polymerization process according to claim 1, where the hydrocarbyl-modified methylaluminoxane contains less than 25 mole percent $AlR^{A1}R^{B1}R^{C1}$ 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 modified-hydrocarbyl methylaluminoxane contains less than 15 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

4. The polymerization process according to claim 1, wherein the aluminum to catalyst metal is less than 500:1.

5. The polymerization process according to claim 1, wherein the aluminum to catalyst metal is less than 200:1 or is less than 50:1.

6. The polymerization process according to claim 1, wherein at least one of R^8 and R^9 is $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, or halogen atom.

7. The polymerization process according to claim 1, wherein at least one of R^8 and R^9 is $(C_1–C_5)$alkyl.

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

9. The polymerization process according to claim 8, wherein R^{42} and R^{47} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$ or R^{43} and R^{46} are (C_1-C_{20})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 (II).

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

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

13. 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 $-Si[(C_1-C_{20})hydrocarbyl]_3$.

14. The polymerization process according to claim 1, wherein R^3 and R^{14} are (C_1-C_{20})alkyl.

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

16. The polymerization process according to claim 1, wherein R3 and R14 are tert-octyl or n-octyl.

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

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

19. The polymerization process according to claim 1, wherein the polymerization process is a solution polymerization reaction.