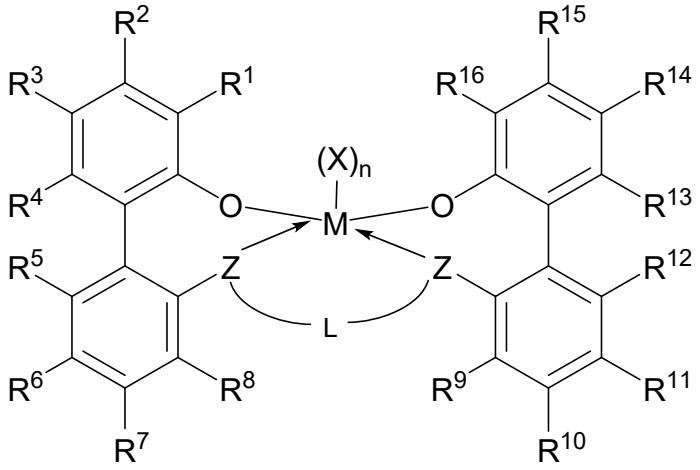
SUMMARY

[0005] 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.

[0006] 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, an activator, and a metal-ligand complex. The hydrocarbyl-modified methylaluminoxane having less than 25 mole percent trialkyl aluminum compound $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum, where R^{A1}, R^{B1}, and R^{C1} are independently linear $(C_1–C_{40})$alkyl, branched $(C_1–C_{40})$alkyl, $(C_1–C_{40})$aryl, or combinations thereof; and one or more metal-ligand complexes comprising a metal–ligand complex according to formula (I):

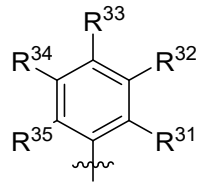


(I)

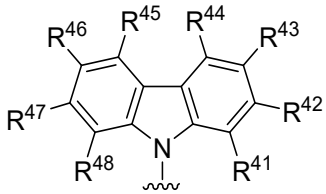
[0007] In formula (I), M is titanium, zirconium, hafnium, scandium, yttrium, or an element of the lanthanide series of the periodic table having a formal oxidation state of +2, +3, or +4. Subscript n of $(X)_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, 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 $–N(R^N)C(O)R^C$. Optionally, two X groups may be linked together. The metal–ligand complex is overall charge-neutral. Each Z is independently chosen from −O−, −S−, $−N(R^N)−$, or $–P(R^P)−$. L is $(C_1–C_{40})$hydrocarbylene or $(C_2–C_{40})$heterohydrocarbylene.

[0008] 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.

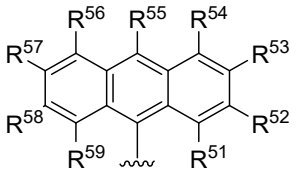
[0009] In formula (I), R^1 and R^{16} are independently selected from the group consisting of –H, $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, −CN, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N=C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)

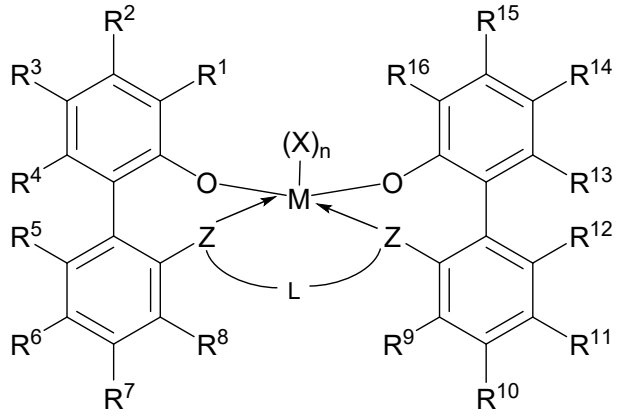


(IV)

[0010] 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.

[0011] 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.

[0011a] 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: 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;

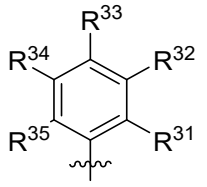
n is 1, 2, or 3;

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;

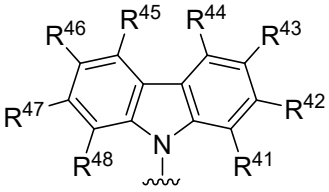
the metal–ligand complex is overall charge-neutral;

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

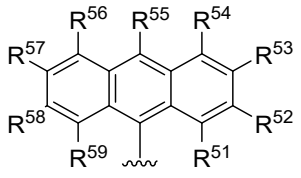
R^1 and R^{16} are independently selected from the group consisting of –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −$Si(R^C)_3$, −$Ge(R^C)_3$, −$P(R^P)_2$, −$N(R^N)_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, $R^CS(O)$−, $R^CS(O)_2$−, −$N{=}C(R^C)_2$, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R^N)$−, $(R^C)_2NC(O)$−, 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, $R^CS(O)$−, $R^CS(O)_2$−, $(R^C)_2C{=}N$−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R^N)$−, $(R^C)_2NC(O)$−, 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 less than 300.

DETAILED DESCRIPTION

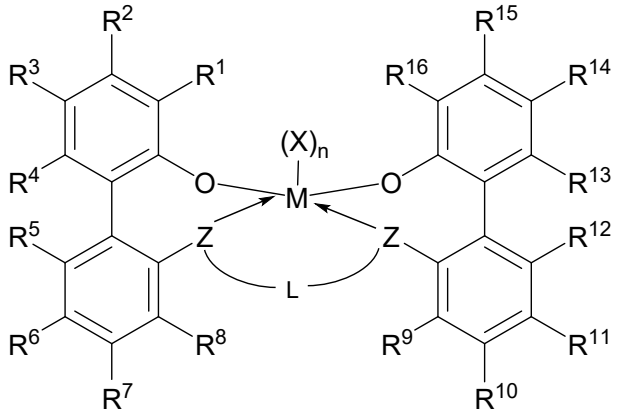
[0012] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided 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.

[0013] Common abbreviations are listed below:

[0014] **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn**: benzyl; ***i*-Pr** : *iso*-propyl; ***t*-Bu** : *tert*-butyl; ***t*-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf** : trifluoromethane sulfonate; **THF** :

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;

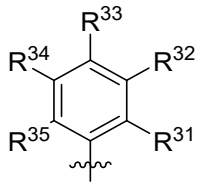
n is 1, 2, or 3;

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;

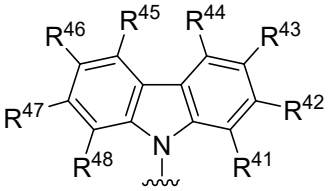
the metal–ligand complex is overall charge-neutral;

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

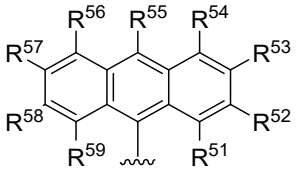
R^1 and R^{16} are independently selected from the group consisting of –H, $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $−Si(R^C)_3$, $−Ge(R^C)_3$, $−P(R^P)_2$, $−N(R^N)_2$, $−OR^C$, $−SR^C$, $−NO_2$, −CN, $−CF_3$, $R^CS(O)−$, $R^CS(O)_2−$, $−N=C(R^C)_2$, $R^CC(O)O−$, $R^COC(O)−$, $R^CC(O)N(R^N)−$,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

2. 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.

3. 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.

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

5. The polymerization process according to claim 4, 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]$_3$.

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

7. The polymerization process according to claim 6, wherein R^{32} and R^{34} are (C_1-C_{12})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 (IV).

9. The polymerization process according to claim 8, wherein at least two of R^{52}, R^{53}, R^{55}, R^{57}, and R^{58} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

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

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

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

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

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

15. 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.

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

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

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