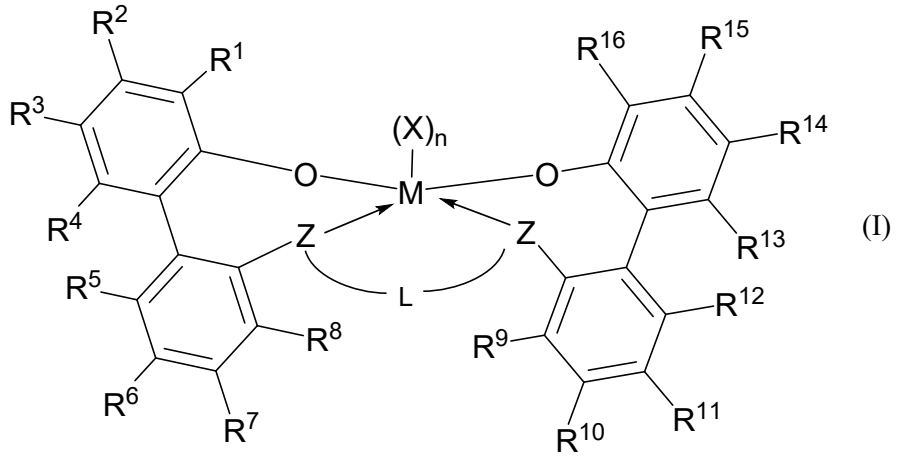
SUMMARY

[0008] There is an ongoing need to create a catalyst system that does not include borate activators while maintaining catalyst efficiency, reactivity, and the ability to produce polymers with good physical properties, specifically a narrow composition distribution of the produced polymer

[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 one or more metal-ligand complexes. The metal–ligand complexes have a structure according to formula (I):

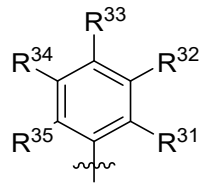


[0010] In formula (I), M is a metal selected from titanium, zirconium, or hafnium. The metal having a formal charge of +1, +2, or +3. Subscript n of $(X)_n$ is 1, 2, or 3. Each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, 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.

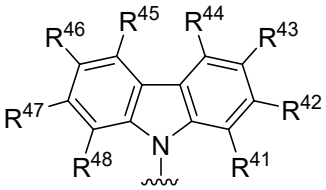
[0011] In formula (I), R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, and R^{15} are independently selected from –H, $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$,

−Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$−OR^C, −SR^C, −NO$_2$, −CN, −CF$_3$, R^{C}S(O)−, R^{C}S(O)$_2$−, (R^C)$_2$C=N−, R^{C}C(O)O−, R^{C}OC(O)−, R^{C}C(O)N(R)−, (R^C)$_2$NC(O)−, and halogen.

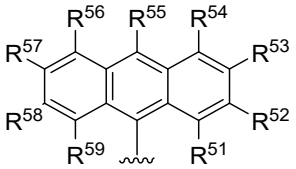
[0012] In formula (I), R^1 and R^{16} are independently selected from the group consisting of –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, −OR^C, −SR^C, −NO$_2$, −CN, −CF$_3$, R^{C}S(O)−, R^{C}S(O)$_2$−, −N=C(R^C)$_2$, R^{C}C(O)O−, R^{C}OC(O)−, R^{C}C(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^{C}S(O)−, R^{C}S(O)$_2$−, (R^C)$_2$C=N−, R^{C}C(O)O−, R^{C}OC(O)−, R^{C}C(O)N(R^N)−, (R^C)$_2$NC(O)−, or halogen.

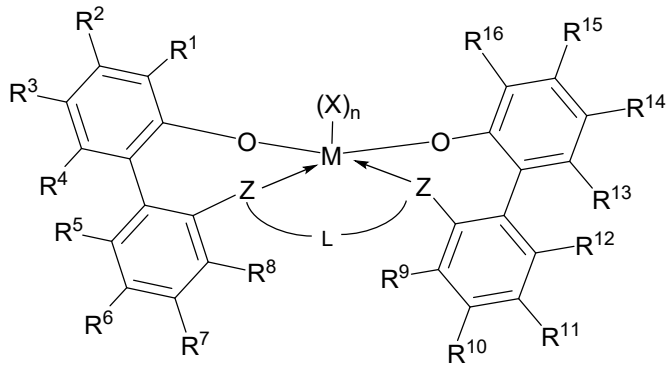
[0014] In formulas (I), (II), (III), and (IV), each R^C, R^P, and R^N is independently a (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl, or −H.

[0015] In some embodiments, the hydrocarbyl-modified methylaluminoxane has less than 50 mole percent trihydrocarbyl aluminum compound Al$R^AR^BR^C$ 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.

[0015a] In one aspect, there is provided a process of polymerizing olefin monomers, the process comprising reacting ethylene and 1-butene in the presence of a catalyst system, wherein the catalyst system comprises:

hydrocarbyl-modified methylaluminoxane; and

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



(I)

where:

M is titanium, zirconium, or hafnium;

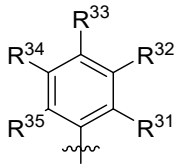
n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from 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 $-NCOR^C$;

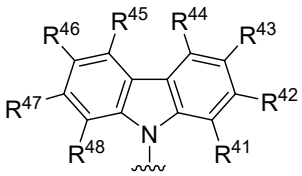
the metal–ligand complex is overall charge-neutral;

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

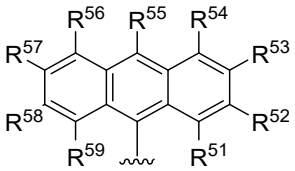
R^1 and R^{16} are independently selected from the group consisting of –H, (C_6–C_{40})aryl, (C_5–C_{40})heteroaryl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where at least one of R^1 and R^{16} is the radical having formula (II) wherein R^{32} and R^{34} are (C_1–C_{12})hydrocarbyl or $-Si[(C_1–C_{20})hydrocarbyl]_3$,

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^{C}S(O)−, R^{C}S(O)$_2$−, (R^C)$_2$C=N−, R^{C}C(O)O−, R^{C}OC(O)−, R^{C}C(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; and

wherein the hydrocarbyl-modified methylaluminoxane comprises less than 50 mole percent trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$ 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, or (C_6−C_{40})aryl;

wherein the hydrocarbyl-modified methylaluminoxane has less than 25 mole percent of the trihydrocarbyl aluminum based on the total moles of the hydrocarbyl-modified methylaluminoxane;

wherein the hydrocarbyl-modified methylaluminoxane is n-octyl modified methylaluminoxane;

wherein the catalysts system does not contain an activator containing boron; and

wherein the polymerization process is a solution polymerization reaction.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 is a Thermal Gradient Interaction Chromatograph (TGIC) with a chromatogram overlay for comparative examples, Entry 1 and Entry 2.

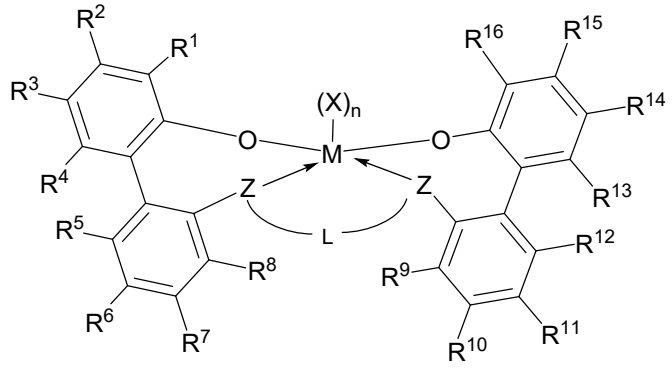
[0017] FIG. 2 is a Thermal Gradient Interaction Chromatograph (TGIC) with a chromatogram overlay for inventive example, Entry 3, and comparative example, Entry 4.

CLAIMS

1. A process of polymerizing olefin monomers, the process comprising reacting ethylene and 1-butene in the presence of a catalyst system, wherein the catalyst system comprises:

hydrocarbyl-modified methylaluminoxane; and

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



(I)

where:

M is titanium, zirconium, or hafnium;

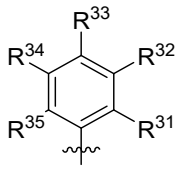
n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from 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 $-NCOR^C$;

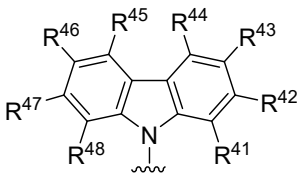
the metal–ligand complex is overall charge-neutral;

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

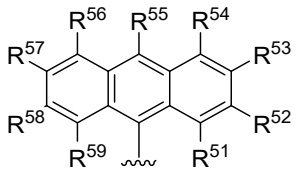
R^1 and R^{16} are independently selected from the group consisting of –H, (C_6–C_{40})aryl, (C_5–C_{40})heteroaryl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where at least one of R^1 and R^{16} is the radical having formula (II) wherein R^{32} and R^{34} are (C_1–C_{12})hydrocarbyl or $-Si[(C_1$–$C_{20})hydrocarbyl]_3$,

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, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, 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; and

wherein the hydrocarbyl-modified methylaluminoxane comprises less than 50 mole percent trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$ 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, or $(C_6–C_{40})$aryl;

wherein the hydrocarbyl-modified methylaluminoxane has less than 25 mole percent of the trihydrocarbyl aluminum based on the total moles of the hydrocarbyl-modified methylaluminoxane;

wherein the hydrocarbyl-modified methylaluminoxane is n-octyl modified methylaluminoxane;

wherein the catalysts system does not contain an activator containing boron; and

wherein the polymerization process is a solution polymerization reaction.

2. The polymerization process according to claim 1, where the hydrocarbyl-modified methylaluminoxane has less than 30 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum.

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

4. 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.

5. The polymerization process according to any of claims 1 to 3, wherein R^8 and R^9 are independently (C_1-C_4)alkyl.

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

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

8. The polymerization process according to any one of claims 1-4, wherein R^6 and R^{11} are *tert*-butyl.

9. The polymerization process according to any one of claims 1 to 4, wherein R^3 and R^{14} are methyl, *tert*-octyl or *n*-octyl.

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

11. 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.

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

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

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