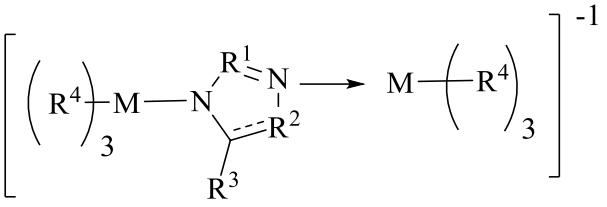
activator in comparison to anion tetrakis(pentafluorophenyl)borate ($^{-}B(C_6F_5)_4$). Activators derived from the non-coordinating anion tetrakis(pentafluorophenyl)borate ($^{-}B(C_6F_5)_4$) capture many of these afore mentioned characteristics. Nevertheless, under typical polymerization reaction conditions, the $^{-}B(C_6F_5)_4$ anion may remain intact in the final polymer. The presence of an intact activator in the final polymer can be deleterious to the electrical properties of the final polymer.

[0011] Activators based on partially hydrolyzed metal trialkyls, such as methylalumoxane (MAO) or modified methylalumoxane (MMAO), for example, decompose more readily than $^{-}B(C_6F_5)_4$ anion, but suffer from poor high-temperature catalyst efficiency and broader compositional and/or molecular weight drift in the final polymer.

[0012] There are ongoing needs for activators that efficiently activate a procatalyst, that are soluble, perform well at high temperature, and do not remain intact in the final polymer. The catalyst systems of this disclosure include, in combination with Group IV metal−ligand complexes as catalysts, activators or co-catalysts that address such needs. In particular, the activators readily react with and activate the Group IV metal−ligand complexes in the production of polyolefin resins, and the polyolefin resins exhibit useful polymer composition and electrical properties. The activators included in the catalyst systems of this disclosure exhibit characteristics, such as, abilities to increase the production of α-olefin polymers, to increase the rate of procatalyst activation, to increase the overall efficiency of the catalyst to enable the catalyst system to operate at high temperatures, to enable the catalyst system to provide consistent polymer composition, and to enable selective deactivation of the activators.

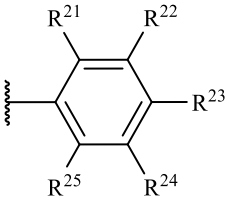
[0013] According to the disclosure, processes for polymerizing olefins include contacting ethylene and a (C_3−C_{40})α-olefin comonomer in the presence of a catalyst system that includes a Group IV metal−ligand complex and a bimetallic activator ionic complex. The bimetallic activator ionic complex includes an anion and a countercation, the anion having a structure according to formula (I):



(I)

[0014] The countercation may be any cation having a formal charge of +1. In formula (I), each M is independently aluminum or boron. R^1 is C(H); and R^2 is selected from $C(R^L)$ or N, wherein each R^L is independently –H, $(C_1–C_{30})$hydrocarbyl, $(C_1–C_{30})$heterohydrocarbyl, or halogen-substituted $(C_1–C_{30})$hydrocarbyl. R^3 is chosen from –H, $(C_1–C_{30})$hydrocarbyl, halogen-substituted $(C_1–C_{30})$hydrocarbyl, $(C_1–C_{30})$heterohydrocarbyl, or $(C_2–C_{30})$hydrocarbylene; R^3 is optionally connected to R^2 to form a ring. When R^3 is –H, R^2 is N or $C(R^L)$, where R^L is $(C_1–C_{30})$hydrocarbyl; and when R^2 is C(H), R^3 is $(C_1–C_{30})$hydrocarbyl.

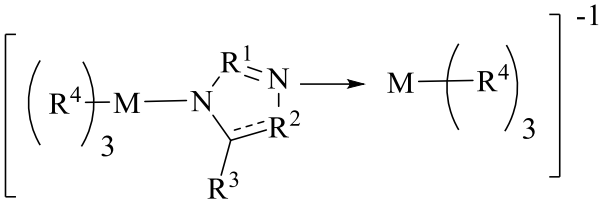
[0015] In formula (I), each R^4 is independently selected from the group consisting of a halogen-substituted $(C_1–C_{30})$alkyl and radicals having formula (II):



(II)

[0016] In formula (II), each R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} is independently chosen from halogen-substituted $(C_1–C_{40})$alkyl, halogen-substituted $(C_6–C_{40})$aryl, –H, $–NR^N_2$, $–OR^C$, $–SR^C$, or halogen. Furthermore, when R^4 is radical according to formula (II), at least three of $R^{21–25}$ are independently chosen from halogen-substituted $(C_1–C_{40})$alkyl, halogen-substituted $(C_6–C_{40})$aryl, or –F. Additionally, when R^4 is a halogen-substituted $(C_1–C_{30})$alkyl, the halogen-substituted $(C_1–C_{30})$alkyl is substituted with at least three halogen atoms. Each R^N and each R^C is independently $(C_1–C_{30})$hydrocarbyl or –H.

[0016a] In one aspect, there is provided a process of polymerizing olefins, the process comprising contacting ethylene and a $(C_3–C_{40})$alpha-olefin comonomer in the presence of a catalyst system comprising a procatalyst and a bimetallic activator complex, the bimetallic activator complex comprising an anion and a countercation, the anion having a structure according to formula (I):



(I)

where:

each M is independently aluminum or boron;

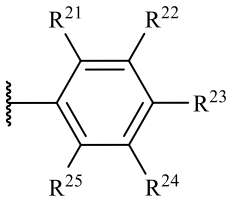
R^1 is C(H);

R^2 is selected from $C(R^L)$, wherein each R^L is independently –H;

R^3 is chosen from $(C_1–C_{30})$hydrocarbyl, $(C_1–C_{30})$heterohydrocarbyl; or

R^3 is connected to R^2 to form a ring;

each R^4 is independently selected from the group consisting of a halogen-substituted $(C_1–C_{30})$alkyl substituted with at least three fluorine atoms, and radicals having formula (II):

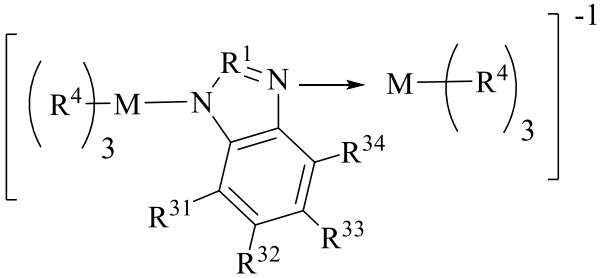


(II)

in which R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} are independently chosen from halogen-substituted $(C_1–C_{40})$alkyl, halogen-substituted $(C_6–C_{40})$aryl, –H, $–NR^N_2$, $–OR^C$, $–SR^C$, or halogen, provided that at least three of $R^{21–25}$ are selected from the group consisting of halogen-substituted $(C_1–C_{40})$alkyl, halogen-substituted $(C_6–C_{40})$aryl, and –F; and

each R^N and each R^C is independently $(C_1–C_{30})$hydrocarbyl or –H;

wherein when R^3 is connected to R^2 to form a ring, the anion of the bimetallic activator complex has a structure according to formula (Ia):



(Ia)

where R^{31}, R^{32}, R^{33}, and R^{34} are independently a (C_1-C_{30})hydrocarbyl, (C_1-C_{30})heterohydrocarbyl, or −H; and R^1, R^4, and M are as defined in formula (I);

and wherein at least one of R^{32} and R^{33} is $-CH_2Si(CH_3)_2(R^C)$, where R^C is independently (C_1-C_{10})alkyl.

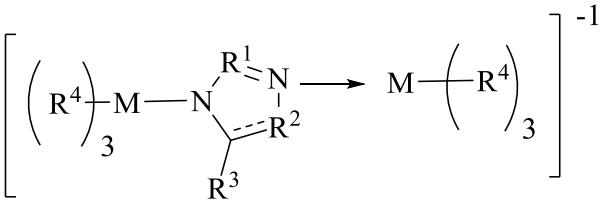
DETAILED DESCRIPTION

[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.

[0018] Common abbreviations are listed below:

CLAIMS

1. A process of polymerizing olefins, the process comprising contacting ethylene and a (C_3–C_{40})alpha-olefin comonomer in the presence of a catalyst system comprising a procatalyst and a bimetallic activator complex, the bimetallic activator complex comprising an anion and a countercation, the anion having a structure according to formula (I):



(I)

where:

each M is independently aluminum or boron;

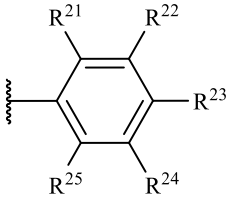
R^1 is C(H);

R^2 is selected from C(R^L), wherein each R^L is independently –H;

R^3 is chosen from (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl; or

R^3 is connected to R^2 to form a ring;

each R^4 is independently selected from the group consisting of a halogen-substituted (C_1–C_{30})alkyl substituted with at least three fluorine atoms, and radicals having formula (II):

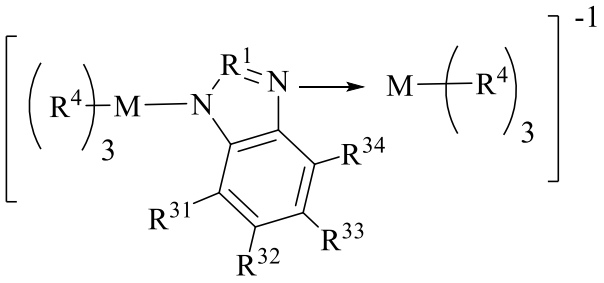


(II)

in which R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} are independently chosen from halogen-substituted (C_1–C_{40})alkyl, halogen-substituted (C_6–C_{40})aryl, –H, –NR^N_2, –OR^C, –SR^C, or halogen, provided that at least three of $R^{21–25}$ are selected from the group consisting of halogen-substituted (C_1–C_{40})alkyl, halogen-substituted (C_6–C_{40})aryl, and –F; and

each R^N and each R^C is independently (C_1−C_{30})hydrocarbyl or –H;

wherein when R^3 is connected to R^2 to form a ring, the anion of the bimetallic activator complex has a structure according to formula (Ia):



(Ia)

where R^{31}, R^{32}, R^{33}, and R^{34} are independently a (C_1−C_{30})hydrocarbyl, (C_1−C_{30})heterohydrocarbyl, or −H; and R^1, R^4, and M are as defined in formula (I);

and wherein at least one of R^{32} and R^{33} is $-CH_2Si(CH_3)_2(R^C)$, where R^C is independently (C_1−C_{10})alkyl.

2. The catalyst system according to claim 1, wherein each R^4 is $-C_6F_5$.

3. The catalyst system according to claim 1 or claim 2, wherein each M is boron.

4. The catalyst system according to any one of claims 1 to 3, wherein R^2 is C(H); and R^3 is (C_1−C_{20})alkyl or (C_1−C_{10})alkyl.

5. The catalyst system according to any one of claims 1 to 3, wherein R^2 is C(H); and R^3 is (C_1−C_{10})alkyl.

6. The catalyst system according to any one of claims 1 to 3, wherein R^2 is C(H); and R^3 is *n*-octyl or *tert*-octyl.

7. The catalyst system according to claim 1, wherein at least one of R^{32} and R^{33} is $-CH_2Si(CH_3)_2(C_8H_{17})$.

8. The catalyst system according to any one of the preceding claims, wherein the procatalyst is a Group IV metal-ligand complex.

9. The catalyst system according to claim 8, wherein the Group IV metal-ligand complex is a bis-biphenylphenoxy metal ligand complex.

10. The catalyst system according to claim 8, wherein the Group IV metal-ligand complex is a constrained-geometry metal ligand complex.