metal complexes. Brønsted acid salts that are fully ionized are capable of transferring a proton to form a cationic derivative of such Group IV metal complexes.

[0006] For activators such as Brønsted acid salts, the cationic component may include cations capable of transferring a hydrogen ion such as ammonium, sulfonium, or phosphonium for example; or oxidizing cations such as ferrocenium, silver (I), or lead (II) cations, for example; or highly Lewis acidic cations such as carbonium or silylium, for example.

[0007] However, once the cations of the activator or co-catalyst activate the procatalyst, the activators may remain in the polymer composition. As a result, the cations and anions may affect the polymer composition. Since not all ions diffuse equally, different ions affect the polymer composition differently. In particular, the size of the ion, the charge of the ion, the interaction of the ion with the surrounding medium, and the dissociation energy of the ion with available counterions will affect the ion's ability to diffuse through a surrounding medium such as a solvent, a gel, or a polymer material.

[0008] Conventional olefin polymerization activators include weakly-coordinating or non-coordinating anions. It has been shown that weak coordination of the anion leads to increased catalytic efficiency of the cationic catalyst. However, since the non-nucleophilic character of the non-coordinating anion also increases diffusion, the residual activator anion in the produced polymer will lower the electrical resistance of the polymer, thereby increasing electrical loss, and thereby decreasing the insulation ability of the produced polymer.

SUMMARY

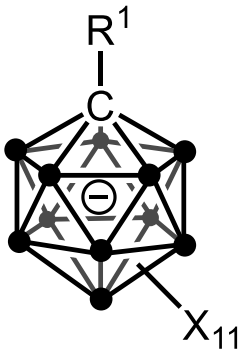
[0009] Ongoing needs exist to create activators or co-catalysts that do not diffuse or negatively affect the polymeric properties of the produced polymer while maintaining the catalytic efficiency of a weakly-coordinating anion. Examples of disclosure include polymerization processes. In one or more examples, the polymerization process includes polymerizing one or more (C_2–C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst to produce a polyolefin and then inserting the anion of the co-catalyst into a polymer chain of the polyolefin. The polyolefin comprises (1) greater than 0 mole percent and less than 1 mole % of the anion of the co-catalyst of the total molar percent of the polyolefin, and (2) a density in the range from 0.853 to 0.920 g/cm^3.

[0009a] In one aspect, there is provided a polymerization process comprising: polymerizing one or more (C_2−C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst in solution to produce a polyolefin; wherein the co-catalyst comprises a cation and a weakly coordinating anion, wherein the anion has a structure having a vinyl terminated alkene, one boron atom or more than one boron atoms, and at least four halogen atoms; and inserting the anion of the co-catalyst into a polymer chain of the polyolefin; wherein the polyolefin comprises: (1) greater than 0 and less than 1 mole % of the anion of the co-catalyst based on the molar composition of the polyolefin, and (2) a density in the range from 0.853 to 0.920 g/cm^3.

[0010] The co-catalyst includes a cation and an anion. The anion has a structure that includes one vinyl terminated alkene, one boron atom or more than one boron atoms, and at least four halogen atoms.

[0011] In examples, the polymer process includes polymerizing one or more (C_2−C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst to produce a polyolefin. Then, the anion of the co-catalyst is inserted into a polymer chain of the polyolefin.

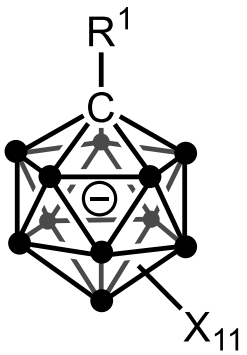
[0012a] In another aspect, there is provided a polymerization process comprising: olymerizing one or more (C_2−C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst to produce a polyolefin; wherein the co-catalyst comprises a cation and an anion, the anion has a structure according to formula (I):



(I)

where R^1 is an unsaturated (C_2−C_{20})hydrocarbyl having a vinyl terminated alkene; and each X is independently a halogen atom; and a boron atom is indicated by a rounded ball; and inserting the anion of the co-catalyst into a polymer chain of the polyolefin.

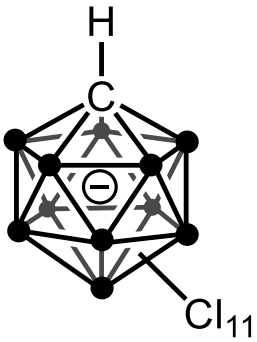
[0012] The co-catalyst comprises a cation and an anion, the anion has a structure according to formula (I):



(I)

[0013] In formula (I), R^1 is an unsaturated (C_2–C_{20})hydrocarbyl having a vinyl terminated alkene; and X is a halogen selected from the groups consisting of fluorine, chlorine, bromine, and iodine.

[0014] In one or more examples, the polyolefin has a dissipation factor less than that of a corresponding polyolefin composition produced under identical polymeric conditions except the molar amount of the anion of formula (I) is replaced by an identical molar amount of a comparative anion having the formula (Ia):



(Ia)

[0015] In some examples, the polymerization process includes copolymerizing ethylene monomer and one or more (C_3–C_{12})α-olefin monomers in the presence of at least one catalyst

and at least one co-catalyst to produce a polyolefin. The anion of the co-catalyst is inserted into a polymer chain of the polyolefin. The polyolefin comprises greater than 0 mole percent and less than 1 mole percent of the anion of the co-catalyst based on the molar composition of the polyolefin.

[0015a] In another aspect, there is provided a polymerization process comprising: copolymerizing ethylene monomer and one or more (C_3–C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst to produce a polyolefin wherein the co-catalyst comprises a cation and an anion, the anion according to formula (II): $^{-}BR^2R^3R^4R^5$ (II) where R^2, R^3, R^4 and R^5 is chosen from (C_1–C_{40})hydrocarbyl, wherein each (C_1–C_{40})hydrocarbyl is substituted with at least one halogen, and wherein at least one (C_1–C_{40})hydrocarbyl is substituted with a vinyl terminated alkene; and inserting the anion of the co-catalyst into a polymer chain of the polyolefin, wherein the polyolefin comprises less than 1 mole percent of the anion of the co-catalyst.

[0016] The co-catalyst comprises a cation and an anion, the anion according to formula (II):

$$^{-}BR^2R^3R^4R^5 \text{ (II)}$$

[0017] In formula (II), R^2, R^3, R^4 and R^5 are independently chosen from (C_1–C_{40})hydrocarbyl. Each (C_1–C_{40})hydrocarbyl is substituted with at least one halogen, and at least one (C_1–C_{40})hydrocarbyl is substituted with a vinyl terminated alkene.

BRIEF DESCRIPTION OF FIGURES

[0018] FIG. 1 is a negative mode mass spectrum from the flow injection analysis of the polyoctene produced from procatalyst P1 and olefin-substituted carborane activator Co-cat. 5.

[0019] FIG. 2 is an expanded mass spectra of around mass to charge ratio (*m/z*) of 786.056 from the negative flow injection analysis of the polyoctene produced from procatalyst P1 and olefin-substituted carborane activator Co.-cat. 5.

[0020] FIG. 3 is a theoretical isotopic modeling of $[C_{20}H_{37}B_{11}Cl_{11}]^{-}$, the product resulting from the polymerization of the anion from Co-Cat 5 and two 1-octene monomer units, in which activated procatalyst P2 is the catalyst.

[0021] FIG. 4 is a negative mode mass spectrum from the flow injection analysis of the polyoctene produced from catalyst P1 and co-catalyst according to embodiments of this disclosure.

[0022] FIG. 5 is a negative mode mass spectrum from the flow injection analysis of the polyoctene produced from catalyst P1 and hydrogen-substituted (no olefin) carborane activator Comp. C3.

[0023] FIG. 6 is a graph of the dissipation factor as a function of frequency for two comparative examples of polyoctene produced from Procatalyst P3 and Comparative Co-Catalysts C1 or C2 and polyoctene produced from Procatalyst P3 and Co-catalysts 1, 2, 3, or 4.

CLAIMS

1. A polymerization process comprising:

polymerizing one or more (C_2–C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst in solution to produce a polyolefin;

wherein the co-catalyst comprises a cation and a weakly coordinating anion,

wherein the anion has a structure having a vinyl terminated alkene, one boron atom or more than one boron atoms, and at least four halogen atoms; and

inserting the anion of the co-catalyst into a polymer chain of the polyolefin;

wherein the polyolefin comprises:

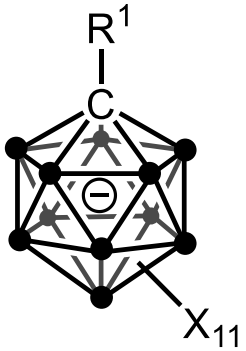
(1) greater than 0 and less than 1 mole % of the anion of the co-catalyst based on the molar composition of the polyolefin, and

(2) a density in the range from 0.853 to 0.920 g/cm^3.

2. A polymerization process comprising:

polymerizing one or more (C_2–C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst to produce a polyolefin;

wherein the co-catalyst comprises a cation and an anion, the anion has a structure according to formula (I):



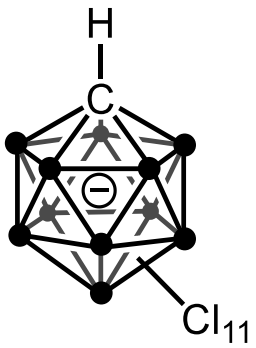
(I)

where R^1 is an unsaturated (C_2–C_{20})hydrocarbyl having a vinyl terminated alkene; and each X is independently a halogen atom; and a boron atom is indicated by a rounded ball; and

inserting the anion of the co-catalyst into a polymer chain of the polyolefin.

3. The process of claim 2, wherein the polyolefin has a dissipation factor less than that of a corresponding polyolefin composition produced under identical polymeric conditions except the

molar amount of the anion of formula (I) is replaced by a comparative anion having the formula (Ia):



(Ia)

4. A polymerization process comprising:

copolymerizing ethylene monomer and one or more (C_3–C_{12})α-olefin monomers in the presence of at least one catalyst and at least one co-catalyst to produce a polyolefin

wherein the co-catalyst comprises a cation and an anion, the anion according to formula (II):

$^{-}BR^2R^3R^4R^5$ (II)

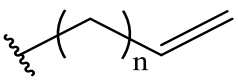
where

R^2, R^3, R^4 and R^5 is chosen from (C_1–C_{40})hydrocarbyl, wherein each (C_1–C_{40})hydrocarbyl is substituted with at least one halogen, and wherein at least one (C_1–C_{40})hydrocarbyl is substituted with a vinyl terminated alkene; and

inserting the anion of the co-catalyst into a polymer chain of the polyolefin,

wherein the polyolefin comprises less than 1 mole percent of the anion of the co-catalyst.

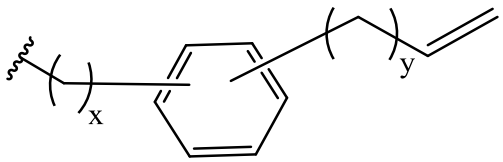
5. The polymerization process of any one of claims 1 – 3, wherein the vinyl terminated alkene has a structure according to formula (III):



(III)

where n is an integer from 1 to 10.

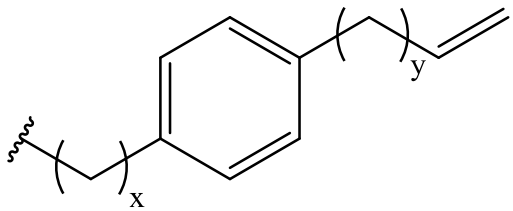
6. The polymerization process of any one of claims 1 – 3, wherein the vinyl terminated alkene has a structure according to formula (V):



(V)

where y is an integer from 1 to 10, and x is 0, 1, 2, and 3.

7. The polymerization process of claim 5, wherein the vinyl terminated alkene according to formula (V) has a structure according to formula (IV):



(IV)

where y and x are as defined in claim 5.

8. The polymerization process of any one of the preceding claims, wherein the ethylene-based polymer has a dissipation factor of less than 0.10 at a frequency of 100 Hz and a temperature of 130 °C or the ethylene-based polymer has a dissipation factor of less than 1.00 at a frequency of 10 Hz and a temperature of 130 °C.

9. The polymerization process of any one of the preceding claims, wherein the ethylene-based polymer has a dissipation factor of less than 10 at a frequency of 1.0 Hz and a temperature of 130 °C or the ethylene-based polymer has a dissipation factor of less than 100 at a frequency of 0.10 Hz and a temperature of 130 °C.

10. The polymerization process of any one of the preceding claims, wherein the cation of the co-catalyst is $^{+}N(H)R^{N}_{3}$, where each R^{N} is chosen from $(C_{1}–C_{20})$alkyl or $(C_{6}–C_{20})$aryl.

11. The polymerization process of any one of the preceding claims, wherein the cation of the co-catalyst is $^{+}N(H)R^{N}_{3}$, where at least two R^{N} are chosen from $(C_{10}–C_{20})$alkyl.

12. The polymerization process of any one of the preceding claims, wherein the cation of the co-catalyst is $^{+}C(C_{6}H_{5})_{3}$.

13. The polymerization process of any one of the preceding claims, wherein the cation of the co-catalyst is $^{+}C(C_6H_4R^C)_3$, where R^C is (C_1-C_{20})alkyl.

14. The polymerization process of any one of claims 1 to 13, wherein the polyolefin is a polyethylene, polyoctene, or an ethylene-based copolymer.

15. The polymerization process of any one of the preceding claims, wherein each X is a chlorine atom.