selectivities, such as different stereoselectivities or monomer selectivities. Under the right conditions, efficient chain shuttling can produce a multi-block copolymer that features a random distribution of hard and soft blocks of random length.

[0004] Even with the advent of CSA and dual catalyst combinations in multi-block copolymer preparation processes, further improvements to said processes can be made. For example, novel catalysts that enable a wider range of processing conditions would be valuable for commercial production.

Summary

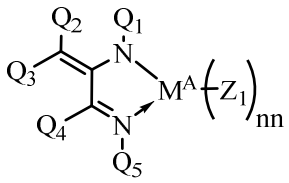
[0005] In certain examples, the present disclosure relates to a composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I):



(I), wherein:

each Z1 independently is $(C_1\text{-}C_{40})$hydrocarbon, $(C_1\text{-}C_{40})$heterohydrocarbon, $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, CN, CF_3, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})_2C{=}N$-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$- , $R^{C1}C(O)N(R)$- , $(R^{C1})_2NC(O)$- , halogen atom, or hydrogen atom;

each R^{C1} independently is $(C_1\text{-}C_{30})$hydrocarbyl or $(C_1\text{-}C_{30})$heterohydrocarbyl;

each M^A independently is a metal of any one of Groups 3 to 6 or Groups 7 to 9 of a Periodic Table of the Elements, the metal being in a formal oxidation state of +2, +3, +4, +5, or +6;

nn is an integer of 1 or 2;

each Q^1 independently is hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl, or $(C_1\text{-}C_{40})$heterohydrocarbyl;

each of Q^2, Q^3, and Q^4 independently is hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$hydrocarbylO-, $(C_1\text{-}C_{40})$hydrocarbylS-, $(C_1\text{-}C_{40})$hydrocarbylS(O)-, $(C_1\text{-}C_{40})$hydrocarbylS$(O)_2$-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_2$N-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_2$P-, or $(C_1\text{-}C_{40})$heterohydrocarbyl;

each Q^5 independently is $(C_1\text{-}C_{40})$hydrocarbyl or $(C_1\text{-}C_{40})$heterohydrocarbyl;

wherein Q^1 and Q^2, Q^2 and Q^3, Q^3 and Q^4, and Q^4 and Q^5 optionally are taken together to form a $(C_1\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or any three or four of Q^1 to Q^5 optionally are taken together to form a respective trivalent or tetravalent analog of $(C_1\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, and the remainder of Q^1 to Q^5, are as defined above;

each of the hydrocarbyl, heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})2C{=}N$-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$-, $R^{C1}C(O)N(R)$-, $(R^{C1})_2NC(O)$-, hydrocarbylene, and heterohydrocarbylene groups independently is unsubstituted or substituted with one or more R^S substituents; and

each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted $(C_1\text{-}C_{18})$alkyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, oxo (i.e., =O), R_3Si-, R_3Ge-, RO-, RS-, RS(O)-, RS$(O)_2$-, R_2P-, R_2N-, $R_2C{=}N$-, NC-, RC(O)O-, ROC(O)- , RC(O)N(R)- , or $R_2NC(O)$- , or two of the R^S are taken together to form an unsubstituted $(C_1\text{-}C_{18})$alkylene, wherein each R independently is an unsubstituted $(C_1\text{-}C_{18})$alkyl; and

optionally, R^{C1} or R^S may have an additional interaction with M^A.

[0006] In certain examples, the present disclosure relates to a composition for use in the polymerization of at least one addition polymerizable monomer to form a multi-block (segmented) copolymer, said copolymer containing therein two or more blocks or segments differing in one or more chemical or physical properties, the composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0007] In certain examples, the present disclosure relates to a composition for use in the polymerization of ethylene and at least one copolymerizable comonomer other than ethylene to form a multi-block (segmented) copolymer, said copolymer containing therein two or more blocks or segments differing in one or more chemical or physical properties, the composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0008] In certain examples, the present disclosure relates to an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

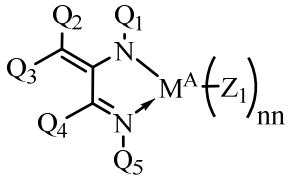
[0008a] In one aspect, the present disclosure refers to an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst (B) comprises a metal-ligand complex of Formula (I):



(I), wherein:

each Z1 independently is (C_1-C_{40})hydrocarbon, (C_1-C_{40})heterohydrocarbon, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, CN, CF_3, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})_2C$=N-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$- , $R^{C1}C(O)N(R)$- , $(R^{C1})_2NC(O)$- , halogen atom, or hydrogen atom;

each R^{C1} independently is (C_1-C_{30})hydrocarbyl or (C_1-C_{30})heterohydrocarbyl;

each M^A independently is a metal of any one of Groups 3 to 6 or Groups 7 to 9 of a Periodic Table of the Elements, the metal being in a formal oxidation state of +2, +3, +4, +5, or +6;

nn is an integer of 1 or 2;

each Q^1 independently is hydrogen, (C_1-C_{40})hydrocarbyl, or (C_1-C_{40})heterohydrocarbyl;

each of Q^2, Q^3, and Q^4 independently is hydrogen, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})hydrocarbylO-, (C_1-C_{40})hydrocarbylS-, (C_1-C_{40})hydrocarbylS(O)-, (C_1-C_{40})hydrocarbylS$(O)_2$-, ((C_1-C_{40})hydrocarbyl)$_2$N-, ((C_1-C_{40})hydrocarbyl)$_2$P-, or (C_1-C_{40})heterohydrocarbyl;

each Q^5 independently is (C_1-C_{40})hydrocarbyl or (C_1-C_{40})heterohydrocarbyl;

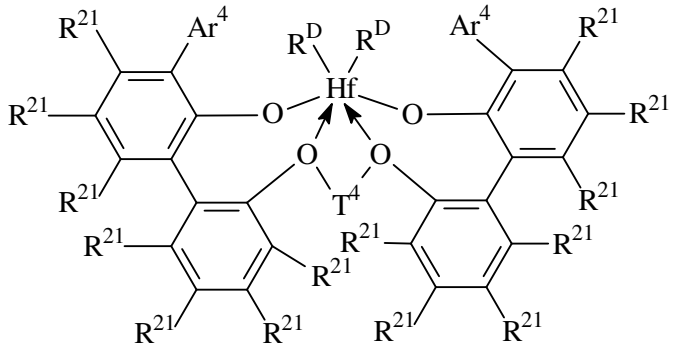
wherein Q^1 and Q^2, Q^2 and Q^3, Q^3 and Q^4, and Q^4 and Q^5 optionally are taken together to form a (C_1-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, or any three or four of Q^1 to Q^5 optionally are taken together to form a respective trivalent or tetravalent analog of (C_1-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, and the remainder of Q^1 to Q^5, are as defined above;

each of the hydrocarbyl, heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})2C$=N-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$-, $R^{C1}C(O)N(R)$-, $(R^{C1})_2NC(O)$-, hydrocarbylene, and heterohydrocarbylene groups independently is unsubstituted or substituted with one or more R^S substituents; and

each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C_1-C_{18})alkyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, oxo (i.e., =O), R_3Si-, R_3Ge-, RO-, RS-, RS(O)-, $RS(O)_2$-, R_2P-, R_2N-, R_2C=N-, NC-, RC(O)O-, ROC(O)- , RC(O)N(R)- , or $R_2NC(O)$- , or two of the R^S are taken together to form an

unsubstituted (C_1-C_{18})alkylene, wherein each R independently is an unsubstituted (C_1-C_{18})alkyl; and

optionally, R^{C1} or R^S may have an additional interaction with M^A; and wherein the first olefin polymerization procatalyst (A) comprises a metal-ligand complex having the following structure:



, wherein:

Ar^4 independently at each occurrence is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, naphthyl, anthracen-5-yl, 1,2,3,4,6,7,8,9-octahydroanthracen-5-yl;

T^4 independently at each occurrence is a propylene-1,3-diyl group, a bis(alkylene)cyclohexan-1,2-diyl group, or an inertly substituted derivative thereof substituted with from 1 to 5 alkyl, aryl or aralkyl substituents having up to 20 carbons each;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen; and

R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group of up to 40 atoms not counting hydrogen.

[0009] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer, said process comprising contacting one or more addition polymerizable monomers under addition polymerizable

conditions with a composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0010] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer comprising ethylene and at least one

copolymerizable comonomer other than ethylene, said process comprising contacting ethylene and one or more addition polymerizable monomers other than ethylene under addition polymerizable conditions with a composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0011] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer, said process comprising contacting one or more addition polymerizable monomers under addition polymerizable conditions with an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0012] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer comprising ethylene and at least one copolymerizable comonomer other than ethylene, said process comprising contacting ethylene and one or more addition polymerizable monomers other than ethylene under addition polymerizable conditions with an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0013] In certain examples, the foregoing processes take the form of continuous solution processes for forming block copolymers, such as multi-block copolymers (preferably linear multi-block copolymers of two or more monomers, especially

ethylene and a C_{3-20} olefin or cycloolefin, and most especially ethylene and a C_{3-20} α-olefin), using multiple catalysts that are incapable of interconversion. That is, the catalysts are chemically distinct. Under continuous solution polymerization conditions, the process is ideally suited for polymerization of mixtures of monomers at high monomer conversions. Under these polymerization conditions, shuttling from the chain shuttling agent to the catalyst becomes advantaged compared to chain growth, and multi-block copolymers, especially linear multi-block copolymers according to the present disclosure, are formed in high efficiency.

[0014] In another example of the present disclosure, there is provided a segmented copolymer (multi-block copolymer), especially a copolymer comprising ethylene in polymerized form, said copolymer containing therein two or more (preferably three or more) segments differing in comonomer content or density or other chemical or physical properties. The copolymer preferably possesses a molecular weight distribution, Mw/Mn, of equal to or less than 10.0 (e.g., equal to or less than 9.0, equal to or less than 8.0, equal to or less than 7.0, equal to or less than 6.0, equal to or less than 5.0, equal to or less than 4.0, equal to or less than 3.0, equal to or less than 2.8, etc.). Most preferably, the polymers of the present disclosure are ethylene multi-block copolymers.

[0015] In yet another example of the present disclosure, there are provided functionalized derivatives of the foregoing segmented or multi-block copolymers.

Brief Description of the Drawings

[0016] FIG. 1 exemplifies the chain shuttling process that occurs in the polymerization processes of the present disclosure.

[0017] FIGS. 2 and 3 provide GPC traces for certain examples of the present disclosure.

Detailed Description

Definitions

[0018] All references to the Periodic Table of the Elements refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless

What is claimed is:

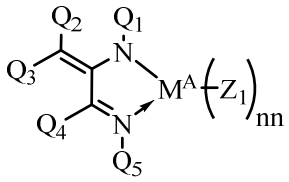
1. An olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst (B) comprises a metal-ligand complex of Formula (I):



(I), wherein:

each Z1 independently is $(C_1\text{-}C_{40})$hydrocarbon, $(C_1\text{-}C_{40})$heterohydrocarbon, $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, CN, CF_3, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})_2C$=N-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$- , $R^{C1}C(O)N(R)$- , $(R^{C1})_2NC(O)$- , halogen atom, or hydrogen atom;

each R^{C1} independently is $(C_1\text{-}C_{30})$hydrocarbyl or $(C_1\text{-}C_{30})$heterohydrocarbyl;

each M^A independently is a metal of any one of Groups 3 to 6 or Groups 7 to 9 of a Periodic Table of the Elements, the metal being in a formal oxidation state of +2, +3, +4, +5, or +6;

nn is an integer of 1 or 2;

each Q^1 independently is hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl, or $(C_1\text{-}C_{40})$heterohydrocarbyl;

each of Q^2, Q^3, and Q^4 independently is hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$hydrocarbylO-, $(C_1\text{-}C_{40})$hydrocarbylS-, $(C_1\text{-}C_{40})$hydrocarbylS(O)-, $(C_1\text{-}C_{40})$hydrocarbylS$(O)_2$-, $((C_1\text{-}C_{40})$hydrocarbyl$)_2$N-, $((C_1\text{-}C_{40})$hydrocarbyl$)_2$P-, or $(C_1\text{-}C_{40})$heterohydrocarbyl;

each Q^5 independently is $(C_1\text{-}C_{40})$hydrocarbyl or $(C_1\text{-}C_{40})$heterohydrocarbyl;

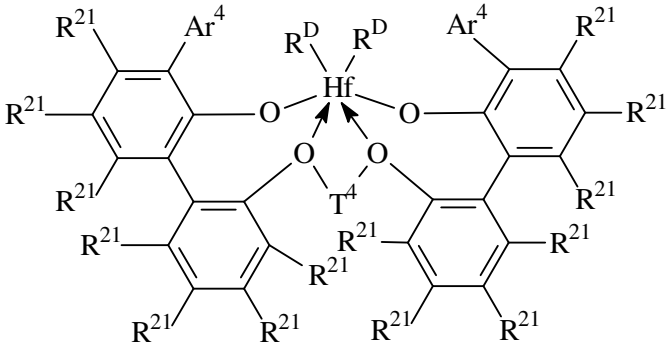
wherein Q^1 and Q^2, Q^2 and Q^3, Q^3 and Q^4, and Q^4 and Q^5 optionally are taken together to form a (C_1-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, or any three or four of Q^1 to Q^5 optionally are taken together to form a respective trivalent or tetravalent analog of (C_1-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, and the remainder of Q^1 to Q^5, are as defined above;

each of the hydrocarbyl, heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})2C=N$-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$-, $R^{C1}C(O)N(R)$-, $(R^{C1})_2NC(O)$-, hydrocarbylene, and heterohydrocarbylene groups independently is unsubstituted or substituted with one or more R^S substituents; and

each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C_1-C_{18})alkyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, oxo (i.e., =O), R_3Si-, R_3Ge-, RO-, RS-, RS(O)-, $RS(O)_2$-, R_2P-, R_2N-, $R_2C=N$-, NC-, RC(O)O-, ROC(O)- , RC(O)N(R)- , or $R_2NC(O)$- , or two of the R^S are taken together to form an unsubstituted (C_1-C_{18})alkylene, wherein each R independently is an unsubstituted (C_1-C_{18})alkyl; and

optionally, R^{C1} or R^S may have an additional interaction with M^A; and

wherein the first olefin polymerization procatalyst (A) comprises a metal-ligand complex having the following structure:



, wherein:

Ar^4 independently at each occurrence is $C_{6\text{-}20}$ aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, naphthyl, anthracen-5-yl, 1,2,3,4,6,7,8,9-octahydroanthracen-5-yl;

T^4 independently at each occurrence is a propylene-1,3-diyl group, a bis(alkylene)cyclohexan-1,2-diyl group, or an inertly substituted derivative thereof substituted with from 1 to 5 alkyl, aryl or aralkyl substituents having up to 20 carbons each;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen; and

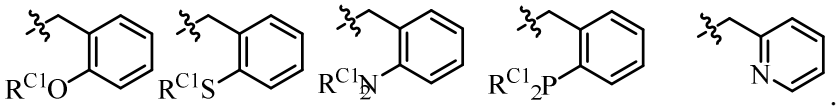
R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group of up to 40 atoms not counting hydrogen.

2. The catalyst system of claim 1, further comprising (D) an activator.

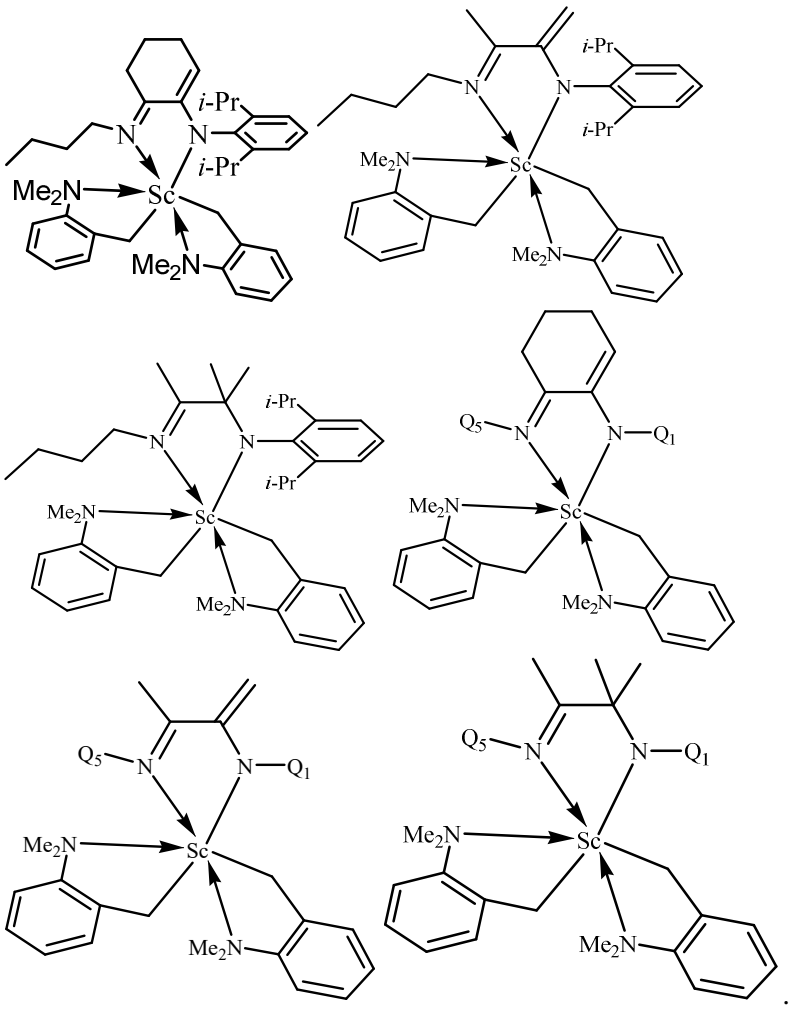
3. The catalyst system of any of the preceding claims, wherein M^A is scandium.

4. The catalyst system of any of the preceding claims, wherein Z1 is $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $Si(R^{C1})_3$, or a hydrido group.

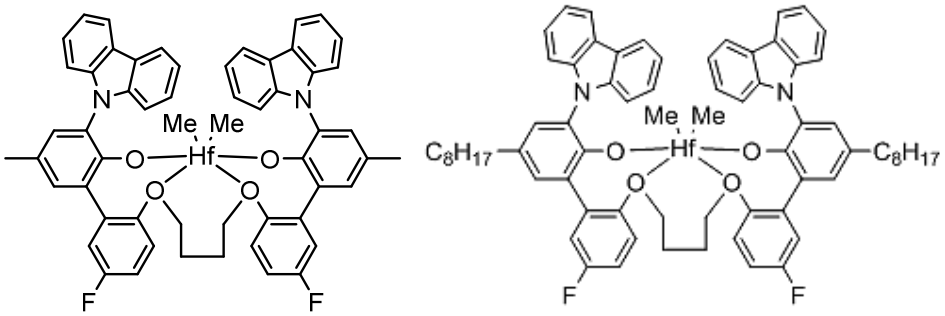
5. The catalyst system of any of the preceding claims, wherein Z1 is selected from the group consisting of:

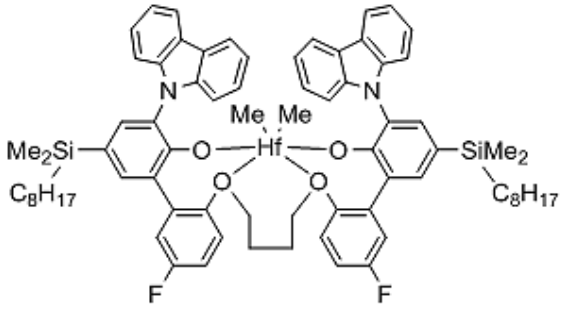


6. The catalyst system of any of the preceding claims, wherein the metal-ligand complex of Formula (I) has the following structure:



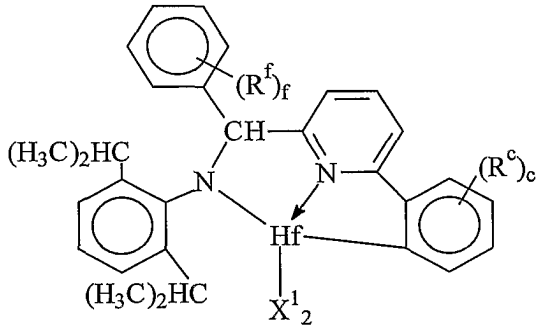
7. The catalyst system of any of the preceding claims, wherein the first olefin polymerization procatalyst (A) comprises a metal-ligand complex selected from the group consisting of:





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8. The catalyst system of any of claims 1-6, wherein the first olefin polymerization procatalyst (A) has the following structure:

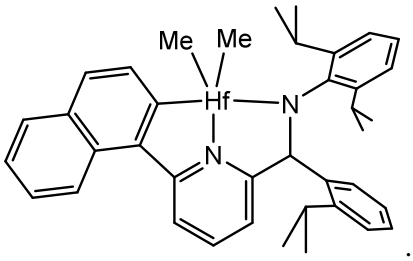


wherein X^1 at each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, and preferably at each occurrence X^1 is methyl;

R^f independently at each occurrence is hydrogen, halogen, C1-20 alkyl, or C6-20 aryl, or two adjacent R^f groups are joined together thereby forming a ring, and f is 1-5; and

R^c independently at each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^c groups are joined together thereby forming a ring, and c is 1-5.

9. The catalyst system of any of claims 1-8, wherein the first olefin polymerization procatalyst (A) has the following structure:


Me
Me
Hf
N
N

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