CLAIMS

1. An olefin polymerization process, the process comprising:

contacting a catalyst composition with an olefin monomer and optionally an olefin comonomer under polymerization conditions to produce an olefin polymer, wherein the catalyst composition comprises:

(i) an *ansa*-metallocene compound having formula (**I**):

$$E(Cp^AR^A{}_m)(Cp^BR^B{}_n)MX_q \quad \textbf{(I)},$$

wherein:

M is Ti, Zr, Hf, Cr, Sc, Y, La, or a lanthanide;

Cp^A and Cp^B independently are a cyclopentadienyl, indenyl, or fluorenyl group;

each R^A and R^B independently is H or a hydrocarbyl, hydrocarbylsilyl, hydrocarbylamino, or hydrocarbyloxide group having up to 18 carbon atoms;

E is a bridging chain of 3 to 8 carbon atoms or 2 to 8 silicon, germanium, or tin atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 18 carbon atoms;

each X independently is F; Cl; Br; I; methyl; benzyl; phenyl; H; BH_4; OBR_2 or SO_3R, wherein R is an alkyl or aryl group having up to 18 carbon atoms; or a hydrocarbyloxide group, a hydrocarbylamino group, or a hydrocarbylsilyl group, any of which having up to 18 carbon atoms;

m is 0, 1, 2, 3, or 4;

n is 0, 1, 2, 3, or 4;

q is 2 when M is Ti, Zr, or Hf; and

q is 1 when M is Cr, Sc, Y, La, or a lanthanide;

(ii) a second metallocene compound; and

(iii) an activator.

2. The process of claim 1, wherein the process is conducted in the presence of added hydrogen, and a Mw/Mn ratio of the olefin polymer decreases as the amount of added hydrogen increases from about 100 to about 500 ppm.

3. The process of claim 2, wherein the process is conducted in the presence of an olefin comonomer at a molar ratio of olefin comonomer to olefin monomer in a range from about 0.01:1 to about 0.25:1.

4. The process of claim 1, wherein the process is conducted in the presence of added hydrogen, and a Mw/Mn ratio of an olefin polymer produced by the process in the presence of 350 ppm added hydrogen is less than a Mw/Mn ratio of an olefin polymer produced by the process under the same polymerization conditions in the presence of 150 ppm added hydrogen.

5. The process of claim 1, wherein:

a Mw of a high molecular weight component of the olefin polymer is reduced by the addition of hydrogen; or

a Mw of a low molecular weight component of the olefin polymer is not reduced by the addition of hydrogen; or

the olefin polymer has less than about 0.002 long chain branches per 1000 total carbon atoms; or

the olefin polymer has an average of from 0 to about 5 short chain branches per 1000 total carbon atoms; or

the olefin polymer has a density of greater than about 0.91 g/cm^3; or

any combination thereof.

6. The process of claim 1, wherein:

M is Ti, Zr, or Hf;

each R^A and R^B independently is H or a hydrocarbyl group having up to 12 carbon atoms;

E is a bridging chain of 3 to 6 carbon atoms or 2 to 4 silicon atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 12 carbon atoms;

each X independently is F, Cl, Br, I, methyl, benzyl, or phenyl;

m is 0, 1, or 2;

n is 0, 1, or 2; and

q is 2.

7. The process of claim 6, wherein:

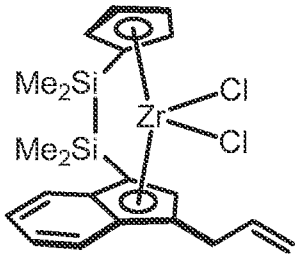
M is Zr or Hf;

Cp^A and Cp^B independently are a cyclopentadienyl or indenyl group;

each R^A and R^B independently is H, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, phenyl, tolyl, or benzyl; and

E is ----$SiMe_2$----$SiMe_2$----.

8. The process of claim 1, wherein the *ansa*-metallocene compound having formula (**I**) comprises:



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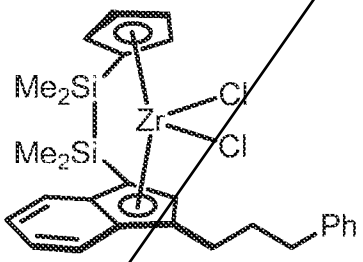

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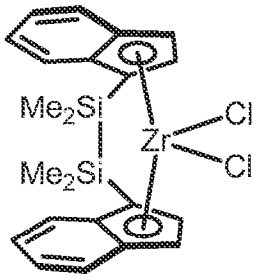

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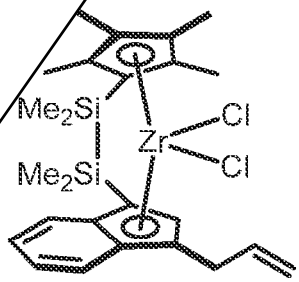

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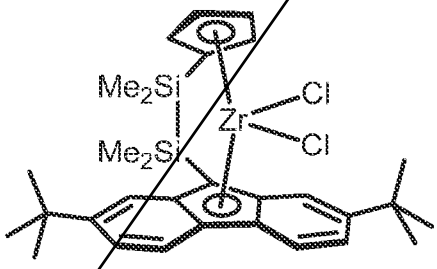


; or a combination thereof.

9. The process of claim 1, wherein the activator comprises an aluminoxane compound, an organoboron or organoborate compound, an ionizing ionic compound, or any combination thereof.

10. The process of claim 1, wherein the activator comprises an activator-support, and wherein the activator-support comprises a solid oxide treated with an electron-withdrawing anion.

11. The process of claim 10, wherein the activator-support comprises fluorided alumina, chlorided alumina, bromided alumina, sulfated alumina, fluorided silica-alumina, chlorided silica-alumina, bromided silica-alumina, sulfated silica-alumina, fluorided silica-zirconia, chlorided silica-zirconia, bromided silica-zirconia, sulfated silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or any combination thereof.

12. The process of claim 11, wherein the catalyst composition further comprises an organoaluminum compound, and wherein the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof.

13. The process of claim 1, wherein the second metallocene compound comprises an unbridged metallocene compound, a bridged metallocene compound, a dinuclear metallocene compound, or a combination thereof.

14. The process of claim 1, wherein the process is conducted in a batch reactor, slurry reactor, gas-phase reactor, solution reactor, high pressure reactor, tubular reactor, autoclave reactor, or a combination thereof.

15. The process of claim 1, wherein the olefin monomer is ethylene, and the olefin comonomer comprises propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, styrene, or a mixture thereof.

16. An olefin polymerization process, the process comprising:

contacting a catalyst composition with an olefin monomer and an olefin comonomer under polymerization conditions to produce an olefin polymer, wherein the catalyst composition comprises:

(i) an *ansa*-metallocene compound having formula (**I**):

$$E(Cp^AR^A_m)(Cp^BR^B_n)MX_q \qquad (\mathbf{I}),$$

wherein:

M is Ti, Zr, Hf, Cr, Sc, Y, La, or a lanthanide;

Cp^A and Cp^B independently are a cyclopentadienyl, indenyl, or fluorenyl group;

each R^A and R^B independently is H or a hydrocarbyl, hydrocarbylsilyl, hydrocarbylamino, or hydrocarbyloxide group having up to 18 carbon atoms;

E is a bridging chain of 3 to 8 carbon atoms or 2 to 8 silicon, germanium, or tin atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 18 carbon atoms;

each X independently is F; Cl; Br; I; methyl; benzyl; phenyl; H; BH_4; OBR_2 or SO_3R, wherein R is an alkyl or aryl group having up to 18 carbon atoms; or a hydrocarbyloxide group, a hydrocarbylamino group, or a hydrocarbylsilyl group, any of which having up to 18 carbon atoms;

m is 0, 1, 2, 3, or 4;

n is 0, 1, 2, 3, or 4;

q is 2 when M is Ti, Zr, or Hf; and

q is 1 when M is Cr, Sc, Y, La, or a lanthanide;

(ii) a second metallocene compound; and

(i) an activator;

wherein the olefin polymer has a conventional comonomer distribution.

17. The process of claim 16, wherein:

M is Zr or Hf;

Cp^A and Cp^B independently are a cyclopentadienyl or indenyl group;

each R^A and R^B independently is H, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, phenyl, tolyl, or benzyl;

E is —$SiMe_2$—$SiMe_2$—;

each X independently is F, Cl, Br, I, methyl, benzyl, or phenyl;

m is 0, 1, or 2;

n is 0, 1, or 2;

q is 2;

the activator comprises an activator-support comprising a solid oxide treated with an electron withdrawing anion;

the process is conducted in the presence of added hydrogen; and

the olefin polymer has:

a bimodal molecular weight distribution; or

less than about 0.002 long chain branches per 1000 total carbon atoms; or

an average of from about 0.5 to about 5 short chain branches per 1000 total carbon atoms; or

a density of greater than about 0.91 g/cm^3; or

any combination thereof.

18. The process of claim 17, wherein the catalyst composition further comprises an organoaluminum compound, and wherein the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof; and

the activator-support comprises fluorided alumina, chlorided alumina, bromided alumina, sulfated alumina, fluorided silica-alumina, chlorided silica-alumina, bromided silica-alumina, sulfated silica-alumina, fluorided silica-zirconia, chlorided silica-zirconia, bromided silica-zirconia, sulfated silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or any combination thereof.

19. The process of claim 18, wherein the olefin monomer is ethylene, and the olefin comonomer comprises propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, styrene, or a mixture thereof.

20. A catalyst composition comprising:

(i) an *ansa*-metallocene compound having formula (**I**):

$$E(Cp^AR^A_m)(Cp^BR^B_n)MX_q \qquad (\mathbf{I}),$$

wherein:

M is Ti, Zr, Hf, Cr, Sc, Y, La, or a lanthanide;

Cp^A and Cp^B independently are a cyclopentadienyl, indenyl, or fluorenyl group;

each R^A and R^B independently is H or a hydrocarbyl, hydrocarbylsilyl, hydrocarbylamino, or hydrocarbyloxide group having up to 18 carbon atoms;

E is a bridging chain of 3 to 8 carbon atoms or 2 to 8 silicon, germanium, or tin atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 18 carbon atoms;

each X independently is F; Cl; Br; I; methyl; benzyl; phenyl; H; BH_4; OBR_2 or SO_3R, wherein R is an alkyl or aryl group having up to 18 carbon atoms; or a hydrocarbyloxide group, a hydrocarbylamino group, or a hydrocarbylsilyl group, any of which having up to 18 carbon atoms;

m is 0, 1, 2, 3, or 4;

n is 0, 1, 2, 3, or 4;

q is 2 when M is Ti, Zr, or Hf; and

q is 1 when M is Cr, Sc, Y, La, or a lanthanide;

(ii) a second metallocene compound; and

(iii) an activator.

CLAIMS

1. An olefin polymerization process, the process comprising:

contacting a catalyst composition with an olefin monomer and optionally an olefin comonomer in the presence of added hydrogen under polymerization conditions to produce an olefin polymer,

wherein the Mw/Mn ratio of the olefin polymer decreases as the amount of added hydrogen increases from about 100 to about 500 ppm, and/or the Mw/Mn ratio of an olefin polymer produced by process in the presence of 350 ppm added hydrogen is less than the Mw/Mn ratio of an olefin polymer produced by the process under the same polymerization conditions in the presence of 150 ppm added hydrogen, and

wherein the catalyst composition comprises:

(i) an ansa-metallocene compound having formula (I):

$$E(Cp^AR^A{}_m)(Cp^BR^B{}_n)MX_q \qquad (I),$$

wherein:

M is Ti, Zr, Hf, Cr, Sc, Y, La, or a lanthanide;

Cp^A and Cp^B independently are a cyclopentadienyl, indenyl, or fluorenyl group;

each R^A and R^B independently is H or a hydrocarbyl, hydrocarbylsilyl, hydrocarbylamino, or hydrocarbyloxide group having up to 18 carbon atoms;

E is a bridging chain of 3 to 8 carbon atoms or 2 to 8 silicon, germanium, or tin atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 18 carbon atoms;

each X independently is F; Cl; Br; I; methyl; benzyl; phenyl; H; BH_4; OBR_2 or SO_3R, wherein R is an alkyl or aryl group having up to 18 carbon atoms; or a hydrocarbyloxide group, a hydrocarbylamino group, or a hydrocarbylsilyl group, any of which having up to 18 carbon atoms;

m is 0, 1, 2, 3, or 4;

n is 0, 1, 2, 3, or 4;

q is 2 when M is Ti, Zr, or Hf; and

q is 1 when M is Cr, Sc, Y, La, or a lanthanide;

(ii) a second metallocene compound; and

(iii) an activator.

2. The process of claim 1, wherein the Mw/Mn ratio of the olefin polymer decreases as the amount of added hydrogen increases from about 100 to about 500 ppm.

3. The process of claim 2, wherein the process is conducted in the presence of an olefin comonomer at a molar ratio of olefin comonomer to olefin monomer in a range from about 0.01:1 to about 0.25:1.

4. The process of claim 1, wherein the Mw/Mn ratio of an olefin polymer produced by the process in the presence of 350 ppm added hydrogen is less than the Mw/Mn ratio of an olefin polymer produced by the process under the same polymerization conditions in the presence of 150 ppm added hydrogen.

5. The process of claim 1, wherein:

the Mw of a high molecular weight component of the olefin polymer is reduced by the addition of hydrogen; or

the Mw of a low molecular weight component of the olefin polymer is not reduced by the addition of hydrogen; or

the olefin polymer has less than about 0.002 long chain branches per 1000 total carbon atoms; or

the olefin polymer has an average of from 0 to about 5 short chain branches per 1000 total carbon atoms; or

the olefin polymer has a density of greater than about 0.91 g/cm^3; or

any combination thereof.

6. The process of claim 1, wherein:

M is Ti, Zr, or Hf;

each R^A and R^B independently is H or a hydrocarbyl group having up to 12 carbon atoms;

E is a bridging chain of 3 to 6 carbon atoms or 2 to 4 silicon atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 12 carbon atoms;

each X independently is F, Cl, Br, I, methyl, benzyl, or phenyl;

m is 0, 1, or 2;

n is 0, 1, or 2; and

q is 2.

7. The process of claim 6, wherein:

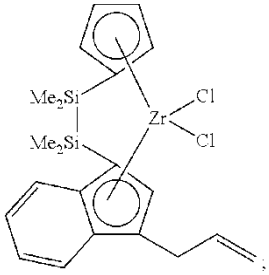
M is Zr or Hf;

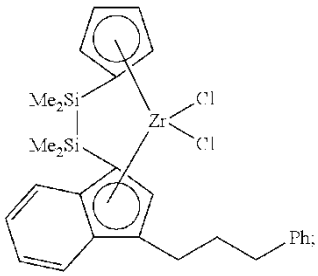
Cp^A and Cp^B independently are a cyclopentadienyl or indenyl group;

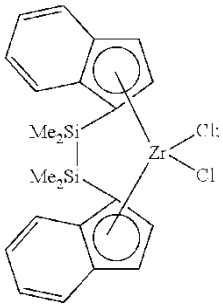
each R^A and R^B independently is H, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, phenyl, tolyl, or benzyl; and

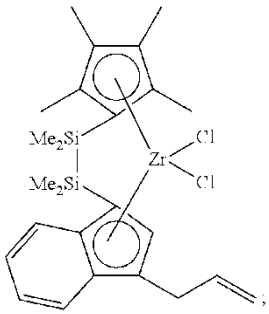
E is —$SiMe_2$-$SiMe_2$-.

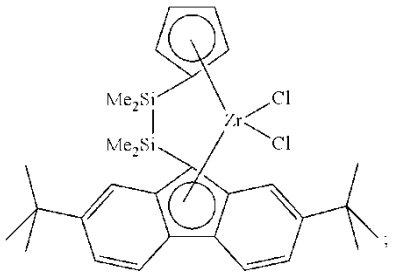
8. The process of claim 1, wherein the ansa-metallocene compound having formula (I) comprises:











or a combination thereof.

9. The process of claim 1, wherein the activator comprises an aluminoxane compound, an organoboron or organoborate compound, an ionizing ionic compound, or any combination thereof.

10. The process of claim 1, wherein the activator comprises an activator-support, and wherein the activator-support comprises a solid oxide treated with an electron-withdrawing anion.

11. The process of claim 10, wherein the activator-support comprises fluorided alumina, chlorided alumina, bromided alumina, sulfated alumina, fluorided silica-alumina, chlorided silica-alumina, bromided silica-alumina, sulfated silica-alumina, fluorided silica-zirconia, chlorided silica-zirconia, bromided silica-zirconia, sulfated silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or any combination thereof.

12. The process of claim 11, wherein the catalyst composition further comprises an organoaluminum compound, and wherein the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof.

13. The process of claim 1, wherein the second metallocene compound comprises an unbridged metallocene compound, a bridged metallocene compound, a dinuclear metallocene compound, or a combination thereof.

14. The process of claim 1, wherein the process is conducted in a batch reactor, slurry reactor, gas-phase reactor, solution reactor, high pressure reactor, tubular reactor, autoclave reactor, or a combination thereof.

15. The process of claim 1, wherein the olefin monomer is ethylene, and the olefin comonomer comprises propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, styrene, or a mixture thereof.

16. An olefin polymerization process, the process comprising:

contacting a catalyst composition with an olefin monomer and an olefin comonomer under polymerization conditions to produce an olefin polymer, wherein the catalyst composition comprises:

(i) an ansa-metallocene compound having formula (I):

$$E(Cp^AR^A{}_m)(Cp^BR^B{}_n)MX_q \qquad (I),$$

wherein:

M is Ti, Zr, Hf, Cr, Sc, Y, La, or a lanthanide;

Cp^A and Cp^B independently are a cyclopentadienyl, indenyl, or fluorenyl group;

each R^A and R^B independently is H or a hydrocarbyl, hydrocarbylsilyl, hydrocarbylamino, or hydrocarbyloxide group having up to 18 carbon atoms;

E is a bridging chain of 3 to 8 carbon atoms or 2 to 8 silicon, germanium, or tin atoms, wherein any substituents on atoms of the bridging chain independently are H or a hydrocarbyl group having up to 18 carbon atoms;

each X independently is F; Cl; Br; I; methyl; benzyl; phenyl; H; BH_4; OBR_2 or SO_3R, wherein R is an alkyl or aryl group having up to 18 carbon atoms; or a hydrocarbyloxide group, a hydrocarbylamino group, or a hydrocarbylsilyl group, any of which having up to 18 carbon atoms;

m is 0, 1, 2, 3, or 4;

n is 0, 1, 2, 3, or 4;

q is 2 when M is Ti, Zr, or Hf; and

q is 1 when M is Cr, Sc, Y, La, or a lanthanide;

(ii) a second metallocene compound; and

(i) an activator;

wherein the olefin polymer has more short chain branches at Mn than at Mw.

17. The process of claim 16, wherein:

M is Zr or Hf;

Cp^A and Cp^B independently are a cyclopentadienyl or indenyl group;

each R^A and R^B independently is H, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, phenyl, tolyl, or benzyl;

E is —$SiMe_2$-$SiMe_2$-;

each X independently is F, Cl, Br, I, methyl, benzyl, or phenyl;

m is 0, 1, or 2;

n is 0, 1, or 2;

q is 2;

the activator comprises an activator-support comprising a solid oxide treated with an electron withdrawing anion;

the process is conducted in the presence of added hydrogen; and

the olefin polymer has:

a bimodal molecular weight distribution; or

less than about 0.002 long chain branches per 1000 total carbon atoms; or

an average of from about 0.5 to about 5 short chain branches per 1000 total carbon atoms; or

a density of greater than about 0.91 g/cm^3; or

any combination thereof.

18. The process of claim 17, wherein the catalyst composition further comprises an organoaluminum compound, and wherein the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof; and the activator-support comprises fluorided alumina, chlorided alumina, bromided alumina, sulfated alumina, fluorided silica-alumina, chlorided silica-alumina, bromided silica-alumina, sulfated silica-alumina, fluorided silica-zirconia, chlorided silica-zirconia, bromided silica-zirconia, sulfated silica-zirconia, fluorided silica-titania, fluorided silica-coated alumina, sulfated silica-coated alumina, phosphated silica-coated alumina, or any combination thereof.

19. The process of claim 18, wherein the olefin monomer is ethylene, and the olefin comonomer comprises propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, styrene, or a mixture thereof.

20. An olefin polymerization process, the process comprising:

contacting a catalyst composition with an olefin monomer and an olefin comonomer in the presence of added hydrogen under polymerization conditions to produce an olefin polymer,

wherein the Mw/Mn ratio of the olefin polymer decreases as the amount of added hydrogen increases from about 100 to about 500 ppm, and/or the Mw/Mn ratio of an olefin polymer produced by the process in the presence of 350 ppm added hydrogen is less than the Mw/Mn ratio of an olefin polymer produced by the process under the same polymerization conditions in the presence of 150 ppm added hydrogen, and

wherein the catalyst composition comprises:

(i) an ansa-metallocene compound having formula (I):

$$E(Cp^AR^A{}_m)(Cp^BR^B{}_n)MX_q \qquad (I),$$

wherein:

M is Ti, Zr, or Hf;

Cp^A and Cp^B independently are a cyclopentadienyl, indenyl, or fluorenyl group;

each R^A and R^B independently is H or a hydrocarbyl group having up to 12 carbon atoms;

E is —$SiMe_2$-$SiMe_2$-;

each X independently is F; Cl; Br; I; methyl; benzyl; phenyl; H; BH_4; OBR_2 or SO_3R, wherein R is an alkyl or aryl group having up to 18 carbon atoms; or a hydrocarbyloxide group, a hydrocarbylamino group, or a hydrocarbylsilyl group, any of which having up to 18 carbon atoms;

m is 0, 1, 2, 3, or 4;

n is 0, 1, 2, 3, or 4; and

q is 2;

(ii) a second metallocene compound; and

(iii) an activator.

21. The process of claim 20, wherein:
M is Zr or Hf;

Cp^A and Cp^B independently are a cyclopentadienyl or indenyl group;

each X independently is F, Cl, Br, I, methyl, benzyl, or phenyl;

m is 0, 1, or 2;

n is 0, 1, or 2;

the olefin monomer is ethylene; and

the olefin comonomer comprises 1-butene, 1-hexene, 1-octene, or a mixture thereof.

22. The process of claim 21, wherein:

the process is conducted in a slurry reactor, gas-phase reactor, solution reactor, or a combination thereof; and

the second metallocene compound comprises an unbridged metallocene compound.

23. The process of claim 21, wherein:

the process is conducted in a slurry reactor, gas-phase reactor, solution reactor, or a combination thereof; and

the second metallocene compound comprises a bridged metallocene compound.

24. The process of claim 21, wherein the activator comprises an aluminoxane compound, an organoboron or organoborate compound, an ionizing ionic compound, or any combination thereof.

25. The process of claim 21, wherein the activator comprises an activator-support comprising a solid oxide treated with an electron-withdrawing anion.

26. The process of claim 25, wherein the catalyst composition further comprises an organoaluminum compound.

27. The process of claim 21, wherein the olefin polymer has:

less than about 0.005 long chain branches per 1000 total carbon atoms; or

more short chain branches at Mn than at Mw; or

a bimodal molecular weight distribution; or

any combination thereof.