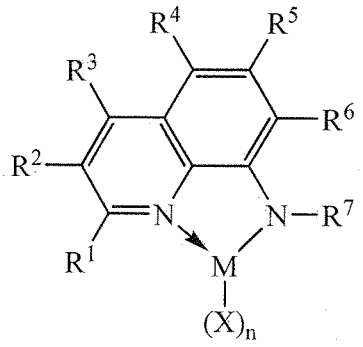
CLAIMS

What is claimed is:

1. A process for polymerizing an olefin monomer, the process comprising a step of contacting together a catalytic amount of a catalyst system, said catalyst system having at least one olefin polymerization catalyst comprising a mixture or reaction product of ingredients (a) and (b), wherein ingredient (a) comprises a metal-ligand complex and ingredient (b) comprises an activating co-catalyst; ~~and~~ an olefin monomer as ingredient (c); and a chain shuttling agent as ingredient (d);

the ingredient (a) being one or more metal-ligand complexes (also referred to herein as precatalysts) of formula (I):



(I)

wherein:

M is a metal of Group 4 of the Periodic Table of the Elements, the metal being in a formal oxidation state of +3 or +4;

n is an integer of from 1 to 5;

Each X independently is a monodentate ligand that is neutral, monoanionic, or dianionic; or two X are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic;

X and n are chosen in such a way that the metal-ligand complex of formula (I) is, in aggregate, neutral;

Each of R^1 to R^6 independently is a hydrogen atom, $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $(C_1\text{-}C_{40})$hydrocarbyl-O-, or halogen atom;

R^7 independently is a $(C_1\text{-}C_{40})$hydrocarbyl or $(C_1\text{-}C_{40})$heterohydrocarbyl;

Or one X, when a monodentate ligand, is taken together with any one of R^1 to R^7 in such a way so that the metal-ligand complex of formula (I) contains a tridentate ligand;

Each of the aforementioned hydrocarbyl and heterohydrocarbyl independently is unsubstituted or substituted with one or more substituents R^S; and

Each R^S independently is a halogen atom, polyfluoro, perfluoro, unsubstituted $(C_1$-$C_{18})$alkyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, R_3Si-, 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 $R_2NC(O)$-, wherein each R independently is an unsubstituted $(C_1$-$C_{18})$alkyl; and

the ingredient (b) being one or more activating co-catalysts, or a reaction product thereof, wherein the ratio of total number of moles of the one or more metal-ligand complexes of formula (I) to total number of moles of the one or more activating co-catalysts is from 1:10,000 to 100:1;

wherein the contacting step is performed under olefin polymerizing conditions and prepares a polyolefin.

2. The process as in claim 1, wherein the metal-ligand complex of formula (I) is characterizedable by any one or more of limitations (a) to (l):

(a) M is hafnium;

(b) n is 3 and each X is a monodentate ligand that is a monoanionic ligand;

(c) at least R^1 is $(C_1$-$C_{40})$hydrocarbyl;

(d) R^7 is a substituted $(C_6$-$C_{40})$aryl;

(e) at least R^3 is $(C_1$-$C_{40})$hydrocarbyl;

(f) the catalyst is characterizedable by a catalyst efficiency of at least 130,000 grams of the polyolefin per gram of metal (M) of the metal-ligand complex of formula (I) when measured at a reaction mixture temperature of 120 degrees Celsius as in Example F1 or 135 degrees Celsius as in Example E;

~~(g) the polyolefin is a poly(ethylene-alpha-olefin) copolymer characterizable with differential scanning calorimetry by a crystallization transition temperature (i.e., T_c) of 60 °C or higher; heat flow versus temperature cooling and heating curves independently exhibiting single peaks for both crystallization and melting transitions, respectively; and either (i) a full width at half maximum peak height in degrees Celsius ($W_{½(DSC)}$) corresponding to a crystallization transition from the DSC cooling curve of less than 5.0 degrees Celsius or (ii) a multiplication product of T_c times $W_{½(DSC)}$ that is less than 500 degrees Celsius squared;~~

~~(h) the polyolefin is a poly(ethylene-alpha-olefin) copolymer characterizable by a polydispersity index of less than 3.0;~~

~~(i) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterizable with proton nuclear magnetic resonance spectroscopy by a mole percent of vinyl groups, expressed as $-CH=CH_2$ groups per 1000 carbon atoms of the polyolefin, of less than 0.10 mole percent;~~

~~(j) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterizable by a weight average molecular weight of at least 500,000 grams per mole as determined by gel permeation chromatography;~~

~~(k) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterizable by a number average molecular weight of at least 170,000 grams per mole as determined by gel permeation chromatography; and~~

~~(l) the process is performed at a reaction temperature of at least 140 degrees Celsius and less than 300 degrees Celsius.~~

3. The process as in claim 1, wherein the polyolefin prepared using the metal-ligand complex of formula (I) is characterized by any one or more of limitations (g) to (l):

(g) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterized~~able~~ with differential scanning calorimetry by a crystallization transition temperature (i.e., T_c) of 60 °C or higher; heat flow versus temperature cooling and heating curves independently exhibiting single peaks for both crystallization and melting transitions, respectively; and either (i) a full width at half maximum peak height in degrees Celsius ($W_{½(DSC)}$) corresponding to a crystallization transition from the DSC cooling curve of less than 5.0 degrees Celsius or (ii) a multiplication product of T_c times $W_{½(DSC)}$ that is less than 500 degrees Celsius squared;

(h) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterized~~able~~ by a polydispersity index of less than 3.0;

(i) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterized~~able~~ with proton nuclear magnetic resonance spectroscopy by a mole percent of vinyl groups, expressed as $-CH=CH_2$ groups per 1000 carbon atoms of the polyolefin, of less than 0.10 mole percent;

(j) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterized~~able~~ by a weight average molecular weight of at least 500,000 grams per mole as determined by gel permeation chromatography;

(k) the polyolefin is a poly(ethylene alpha-olefin) copolymer characterized~~able~~ by a number average molecular weight of at least 170,000 grams per mole as determined by gel permeation chromatography; and

(l) the process is performed at a reaction temperature of at least 140 degrees Celsius and less than 300 degrees Celsius.

~~34~~. The process as in claims 2 and 3, the process being characterized~~able~~ by at least each of limitations (a) to (c) and limitation (d); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (e) and, optionally, limitation (d); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (f) and, optionally, limitation (d) or (e), or limitations (d) and (e); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (g) and, optionally, limitation (d), (e), or (f) or limitations (d), (e) and (f); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (h) and, optionally, limitation (d), (e), (f), or (g) or limitations (d), (e), (f) and (g); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (i) and, optionally, limitation (d), (e), (f), (g), or (h) or limitations (d), (e), (f), (g) and (h); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (j) and, optionally, limitation (d), (e), (f), (g), (h), or (i) or limitations (d), (e), (f), (g), (h) and (i); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (k) and, optionally, limitation (d), (e), (f), (g), (h), (i), or (j) or limitations (d), (e), (f), (g), (h), (i) and (j); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (k) and, optionally, limitation (d), (e), (f), (g), (h), (i), (j), or (k) or limitations (d), (e), (f), (g), (h), (i), (j) and (k); or

~~The process being characterizable by~~ at least each of limitations (a) to (c) and limitation (k) and, optionally, limitation (d), (e), (f), (g), (h), (i), (j), (k), or (l) or limitations (d), (e), (f), (g), (h), (i), (j), (k) and (l).

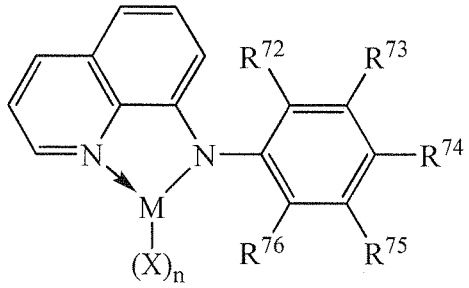
45. The process as in any one of claims 2 to ~~4or 3~~, the polyolefin being the poly(ethylene alpha-olefin) copolymer, the poly(ethylene alpha-olefin) copolymer being characterizedable by at least a combination comprising a polydispersity index of less than 3.0; single peaks observed in both the DSC heating and cooling curves; and $W_{½(DSC)}$ less than 5.0 degrees Celsius; or

the polyolefin being the poly(ethylene alpha-olefin) copolymer, the poly(ethylene alpha-olefin) copolymer being characterizedable by at least a combination comprising a polydispersity index of less than 2.5; $W_{½(DSC)}$ less than 4.0 degrees Celsius; and the mole percent vinyl groups is less than 0.03 mole percent; or

the polyolefin being the poly(ethylene alpha-olefin) copolymer, the poly(ethylene alpha-olefin) copolymer being characterizedable by at least a combination comprising a polydispersity index of less than 3.0; single peaks observed in both the DSC heating and cooling curves; and $T_c*W_{½(DSC)}$ less than 500 degrees Celsius squared; or

the polyolefin being the poly(ethylene alpha-olefin) copolymer, the poly(ethylene alpha-olefin) copolymer being characterizedable by at least a combination comprising a polydispersity index of less than 2.5; $T_c*W_{½(DSC)}$ less than 400 degrees Celsius squared; and the mole percent vinyl groups is less than 0.03 mole percent.

~~5~~6. The process as in any one of claims 1 to 45, wherein the metal-ligand complex of formula (I) is a metal-ligand complex of formula (Ip), (Ia), (Ia-1), (Ia-1.1), or (Ia-2):

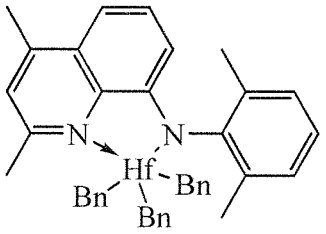


(Ia-1.2)

67. The process as in claim 56, wherein at least one of R^{72} and R^{76} independently is a $(C_1\text{-}C_{40})$alkyl.

78. The process as in any one of claims 1 to 67, wherein R^1 is $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $(C_1\text{-}C_{40})$hydrocarbyl-O-, or halogen atom.

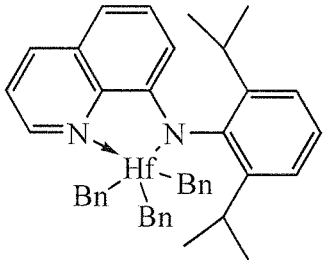
89. The process as in claim 56, wherein the metal-ligand complex of formula (Ia-1.1) is metal-ligand complex (8):



(8)

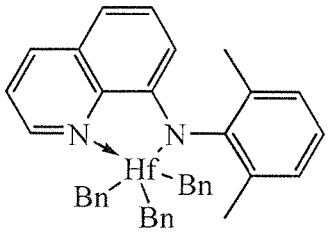
; and

wherein the metal-ligand complex of formula (Ia-1.2) is any one of metal-ligand complexes (5) to (7) and (10):



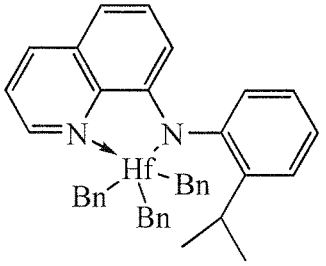
(5)

;

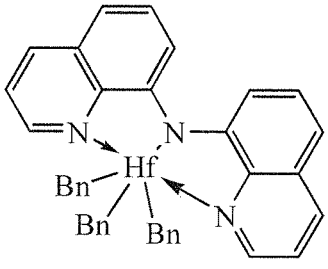


(6)

;



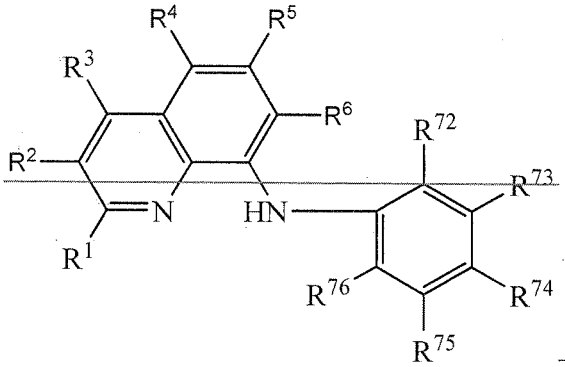
(7)



(10)

; and

9. A ligand of formula (Qp):



(Qp)

or a Group 1 or 2 metal salt thereof, wherein the Group 1 or 2 metal of the Group 1 or 2 metal salt is a cation of any one of the metals of Groups 1 and 2 of the Periodic Table of the Elements;

Each of R^1 to R^6 independently is a hydrogen atom, $(C_1$-$C_{40})$hydrocarbyl, $(C_1$-$C_{40})$heterohydrocarbyl, $(C_1$-$C_{40})$hydrocarbyl-O-, or halogen atom;

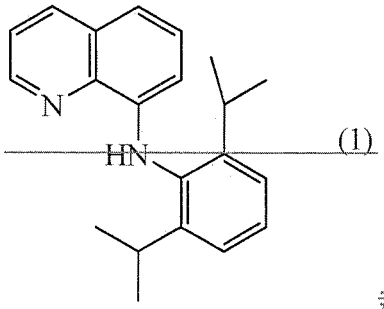
At least one of R^{72} and R^{76} independently is a $(C_1$-$C_{40})$alkyl and each of the remainder of R^{72} to R^{76} independently is a hydrogen atom or R^S, wherein R^S is as defined previously;

Each of the aforementioned hydrocarbyl (e.g., $(C_1$-$C_{40})$hydrocarbyl) and heterohydrocarbyl independently is unsubstituted or substituted with one or more substituents R^S; and

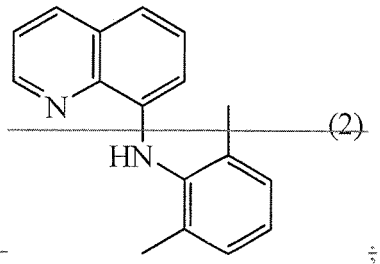
Each R^S independently is a halogen atom, polyfluoro, perfluoro, unsubstituted $(C_1$-$C_{18})$alkyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, R_3Si-, RO-, RS-, RS(O)-, $RS(O)_2$-, R_2P-, R_2N-, R_2C=N-, NC-, RC(O)O-, ROC(O)-,

~~$RC(O)N(R)_2$, or $R_2NC(O)$, wherein each R independently is an unsubstituted (C_1-C_{18})alkyl.~~

~~10. The ligand as in claim 9, wherein the ligand of formula (Qp) is any one of ligands (1) to (4):~~

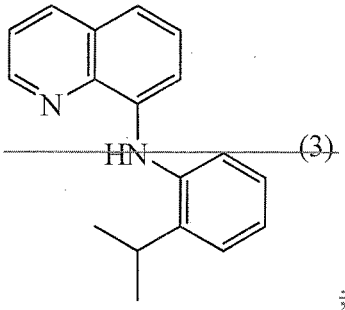


~~(1)~~

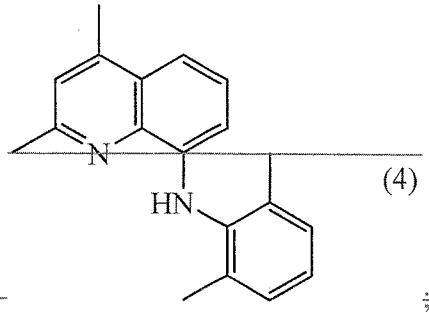


~~(2)~~

~~;~~ ~~;~~



~~(3)~~



~~(4)~~

~~; and~~ ~~; or a Group 1 or 2 metal salt thereof, wherein the Group 1 or 2 metal of the Group 1 or 2 metal salt is a cation of any one of the metals of Groups 1 and 2 of the Periodic Table of the Elements.~~