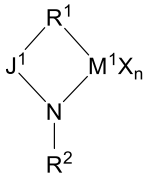
CLAIMS

1. A process to form a composition comprising an ethylene/vinylarene diblock interpolymer and/or an ethylene/vinylarene triblock interpolymer, said process comprising at least the following steps:

A) polymerizing in a reactor A, a mixture A comprising ethylene, and optionally an alpha-olefin, and optionally a vinylarene, in the presence of at least the following: a) a metal complex S selected from the following: Formula S1, Formula S2, Formula S3, Formula S4, or Formula S5:



(Formula S1),

wherein M^1 is a metal selected from titanium (Ti), zirconium (Zr), or hafnium (Hf); and wherein the metal is in a formal oxidation state of +2, +3, or +4;

each X is independently selected from a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and wherein each X is independently a monodentate ligand or a bidentate ligand;

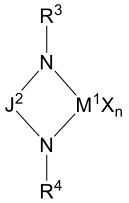
n is 0, 1, or 2, and optionally when n is 1, X may be a bidentate ligand;

R^1 is a bridging group comprising from 2 to 41 atoms other than hydrogen, and wherein, optionally, the bond between R^1 and M is a pi bond;

R^2 is selected from a substituted or an unsubstituted (C_1-C_{30})hydrocarbyl group, or a substituted or an unsubstituted (C_1-C_{30})heterohydrocarbyl group;

J^1 is a bridging group linking N and R^1, and comprising from 2 to 40 atoms other than hydrogen, and wherein, optionally, the bridging group comprises a N atom that can interact with the metal (M^1) via an electron donative bond; and

wherein the metal complex is overall charge-neutral;



(Formula S2),

wherein M^1 is a metal selected from titanium (Ti), zirconium (Zr), or hafnium (Hf); and where the metal is in a formal oxidation state of +2, +3, or +4;

each X is independently selected from a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl or −H; and wherein each X is

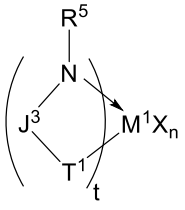
independently a monodentate or a bidentate ligand;

n is 0, 1, or 2, and optionally when n is 1, X may be a bidentate ligand;

each of R^3 and R^4 is independently selected from a substituted or an unsubstituted (C_6-C_{20})aryl group, or a substituted or an unsubstituted (C_5-C_{20})heteroaryl group;

N and N are linked by a bridging group, J^2, which comprises from 2 to 40 atoms other than hydrogen, and wherein, optionally, the bridging group comprises a N atom that can interact with the metal via an electron donative bond; and

wherein the metal complex is overall charge-neutral;



(Formula S3),

wherein M^1 is a metal selected from titanium (Ti), zirconium (Zr), or hafnium (Hf); and wherein the metal is in a formal oxidation state of +2, +3, or +4;

each X is independently selected from a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, substituted, a unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and wherein each X is independently a monodentate ligand or a bidentate ligand;

n is 0, 1, or 2, and optionally when n is 1, X may be a bidentate ligand;

R^5 is a substituted or unsubstituted (C_1-C_{30})hydrocarbyl group, or a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl group, $-Si(R^C)_3$, or −H;

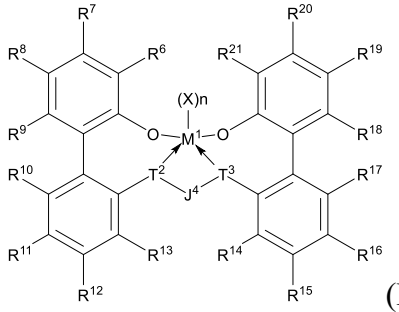
T^1 is selected from −O−, −S−, $-N(R^N)-$, or $-P(R^P)-$;

t is 1 or 2;

and wherein T^1 and N are linked by a bridging group, denoted by J^3, which comprises from 4 to 50 atoms other than hydrogen;

wherein each R^P, R^N, and R^C in Formula S3 is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and

wherein the metal complex is overall charge-neutral;



(Formula S4),

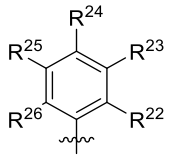
wherein M^1 is a metal selected from zirconium (Zr) or hafnium (Hf); and wherein the metal is in a formal oxidation state of +2, +3, or +4;

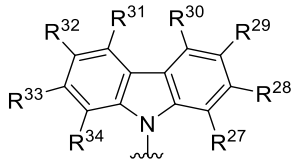
each X is independently selected from a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{30})$heterohydrocarbyl, or −H; and wherein each X is independently a monodentate ligand or a bidentate ligand;

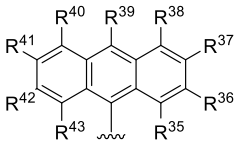
n is 0, 1, or 2, and optionally when n is 1, X may be a bidentate ligand;

each of -T^2- and -T^3- is independently selected from −O−, −S−, −N(R^N)−, or –P(R^P)−;

R^6 and R^{21} are each independently selected from the group consisting of –H, a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, R^CS(O)−, R^CS(O)$_2$−, (R^C)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R)−, (R^C)$_2$NC(O)−, halogen, radicals having formula (I), radicals having formula (II), and radicals having formula (III):



(I),


(II),


(III),

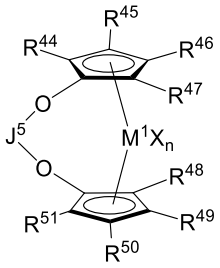
where each of $R^{22–26}$, $R^{27–34}$, and $R^{35–43}$ is independently selected from a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, −N=CHR^C, −OR^C, −SR^C, −NO_2, −CN, −CF_3, R^CS(O)−, R^CS(O)$_2$−, (R^C)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R^N)−, (R^C)$_2$NC(O)−, halogen, or –H;

each of $R^{7–20}$ is independently selected from a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, −N=CHR^C, −OR^C, −SR^C, −NO_2, −CN, −CF_3, R^CS(O)−, R^CS(O)$_2$−, (R^C)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R^N)−, (R^C)$_2$NC(O)−, halogen, or −H;

J^4 is a substituted or unsubstituted $(C_1\text{−}C_{40})$hydrocarbylene or a substituted or unsubstituted $(C_1\text{−}C_{40})$heterohydrocarbylene, wherein the substituted or unsubstituted $(C_1\text{−}C_{40})$hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom

linker backbone, linking the groups T^2 and T^3 in Formula S4 (to which J^4 is bonded); or the substituted or unsubstituted (C_1–C_{40})heterohydrocarbylene has a portion that comprises a 1-atom to 10-atom linker backbone, linking the groups T^2 and T^3 in Formula S4, wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone, independently, is a carbon atom or a heteroatom of a heteroatom group, wherein each heteroatom group is independently O, S, S(O), $S(O)_2$, $Si(R^C)_2$, $Ge(R^C)_2$, $P(R^C)$, or $N(R^C)$, wherein each R^C is independently a substituted or unsubstituted (C_1–C_{30})hydrocarbyl or a substituted or unsubstituted (C_1–C_{30})heterohydrocarbyl; and wherein each R^P, R^N, and remaining R^C in Formula S4 is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and

wherein the metal complex is overall charge-neutral; or



(Formula S5),

wherein M^1 is a metal selected from titanium (Ti), zirconium (Zr), or hafnium (Hf); and wherein the metal is in a formal oxidation state of +2, +3, or +4;

each X is independently selected from a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and wherein each X is independently a monodentate ligand or a bidentate ligand;

n is 0, 1, or 2, and optionally when n is 1, X may be a bidentate ligand;

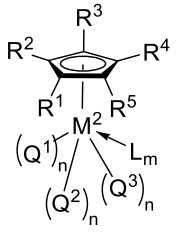
$R^{44\text{-}51}$ are each independently selected from a substituted or unsubstituted (C_1-$_{40}$)hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, or –H; and optionally two or more groups from $R^{44\text{-}51}$ are linked, such that that cyclopentadienyl group is a substituted or unsubstituted indenyl group, or a substituted or unsubstituted fluorenyl group; and wherein R^C is independently selected from a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H;

O and O are linked by a bridging group, denoted by J^5, which comprises from 1 to 30 atoms other than hydrogen; and

wherein the metal complex is overall charge-neutral;

B) polymerizing in a reactor B, a mixture B comprising ethylene, a vinylarene, and

optionally an alpha-olefin, in the presence of at least the following: b) a metal complex H selected from the following Formula H1 or Formula H2:



(Formula H1),

wherein M^2 is Ti, Sc, Y, or an element from the lanthanide series;

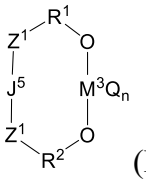
R^1, R^2, R^3, R^4, and R^5 are each independently H or a substituted or unsubstituted hydrocarbyl group, a substituted or unsubstituted heterohydrocarbyl group;

Q^1, Q^2, and Q^3 are each independently a substituted or unsubstituted hydrocarbyl group, a substituted or unsubstituted heterohydrocarbyl group, or a halogen;

L is a Lewis base; and each n is independently 0 or 1; and m is an integer from 0 to 3; and

wherein optionally at least one L group and at least one Q group are connected, and optionally at least one R group and at least one Q group are connected;

wherein the metal complex is overall charge-neutral;



(Formula H2),

wherein M^3 is a metal selected from titanium (Ti), zirconium (Zr), or hafnium (Hf); and wherein the metal is in a formal oxidation state of +2, +3, or +4;

each Q is independently selected from a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and wherein each Q is independently a monodentate ligand or a bidentate ligand;

n is 0, 1, or 2, and optionally when n is 1, Q may be a bidentate ligand;

R^1 and R^2 are each independently a bridging group comprising from 2 to 41 atoms other than hydrogen, and wherein, optionally, R^1 and R^2 each independently may be a substituted or unsubstituted arylene group;

each of -Z^1- and -Z^2- is independently selected from −O−, −S−, −Se−, −N(R^N)−, or –P(R^P)−; and wherein each of -Z^1- and -Z^2- independently can optionally interact with the metal via an electron donative bond;

Z^1 and Z^2 are linked by a bridging group, denoted by J^5, which comprises from 1 to 50

atoms other than hydrogen;

wherein R^P and R^N, are each independently a substituted or unsubstituted (C_1-C_{30})-hydrocarbyl, a substituted or unsubstituted (C_1-C_{30})heterohydrocarbyl, or −H; and

wherein the metal complex is overall charge-neutral; and

wherein step A occurs before step B, and at least a portion of the reactor product in reactor A is transferred to reactor B; or step B occurs before step A, and at least a portion of the reactor product in reactor B is transferred to reactor A; and

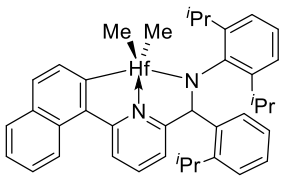
wherein if step A occurs before step B, then at least one chain shuttling agent is fed into the reactor A; and

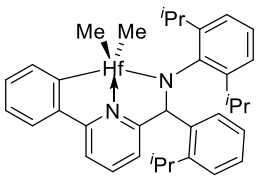
wherein if step B occurs before step A, then at least one chain shuttling agent is fed into the reactor B; and

wherein the vinylarene in step A = the vinylarene in step B; and the alpha-olefin in step A = the alpha-olefin in step B.

2. The process of claim 1, wherein the metal complex S is selected from Formula S1, and the metal complex H is selected from Formula H1.

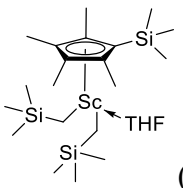
3. The process of claim 1 or claim 2, wherein, the metal complex S is selected from structure s1a1 or structure s1a2:

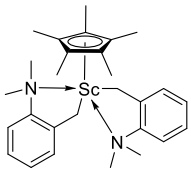


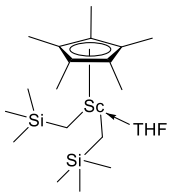
(s1a1) or


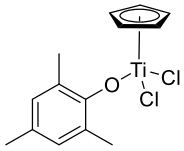
(s1a2).

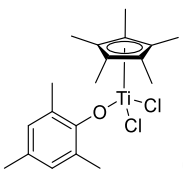
4. The process of any one of claims 1-3, wherein, the metal complex H is selected from the following formulas h1a1, h1a2, h1a3, h1b1, h1b2, h1b3, h2a1 or h2a2 (note: Bn = benzyl group (Ph-CH_2-)):

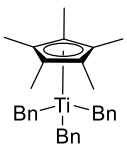


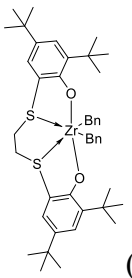
(h1a1),


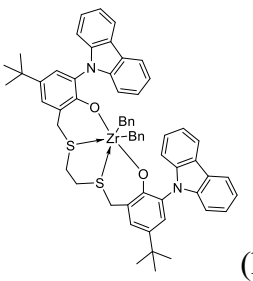
(h1a2),


(h1a3),


(h1b1),


(h1b2),


(h1b3),


(h2a1), or


(h2a2).

5. The process of any one of claims 1-4, wherein the at least one chain shuttling agent is selected from the following: an alkyl zinc compound, an alkyl aluminum compound, a dual headed chain shuttling agent, or a combination thereof.

6. The process of any one of claims 1-5, wherein step A occurs before step B.

7. The process of any one of claims 1-5, wherein step B occurs before step A.

8. The process of any one of claims 1-7, wherein, for the ethylene/vinylarene diblock interpolymer or the ethylene/vinylarene triblock interpolymer, the vinylarene is styrene.

9. The process of any one of claims 1-8, wherein the mixture A comprises the alpha-olefin.

10. A composition comprising an ethylene/vinylarene diblock interpolymer or an ethylene/vinylarene triblock interpolymer, said diblock interpolymer comprising at least one polymer structure selected from Structure 1, as shown below, and said triblock interpolymer comprising at least one polymer structure selected from Structure 2 or Structure 3, each as shown below, where AR refers to vinylarene-rich and AP refers to vinylarene-poor:

(AR)-(AP) (Structure 1),

(AR)-(AP)-(AR) (Structure 2),

(AP)-(AR)-(AP) (Structure 3); and

wherein each (AR) segment independently comprises, in polymerized form, ethylene, the vinylarene and optionally an alpha-olefin; and

wherein each (AP) segment independently comprises, in polymerized form, ethylene, optionally the vinylarene and optionally the alpha-olefin; and

wherein each (AR) segment independently comprises, in polymerized form, > 10 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment; and

wherein each (AP) segment independently comprises, in polymerized form, ≤ 10 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AP) segment.

11. The composition of claim 10, wherein, for the ethylene/vinylarene diblock interpolymer or the ethylene/vinylarene triblock interpolymer, each (AR) segment independently comprises, in polymerized form, from 15 mol% to < 100 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment.

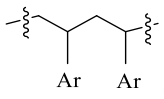
12. The composition of claim 10 or claim 11, wherein, for the ethylene/vinylarene diblock interpolymer or the ethylene/vinylarene triblock interpolymer, each (AP) segment

independently comprises, in polymerized form, from 0 mol% to 10 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AP) segment.

13. The composition of any one of claims 10-12, wherein, for the ethylene/vinylarene diblock interpolymer or the ethylene/vinylarene triblock interpolymer, each (AR) segment independently comprises, in polymerized form, from 2.0 mol% to 80 mol% of ethylene, based on the total moles of polymerized monomers in the (AR) segment.

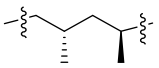
14. The composition of any one of claims 10-13, wherein, for the ethylene/vinylarene diblock interpolymer or the ethylene/vinylarene triblock interpolymer, each (AP) segment independently comprises, in polymerized form, from 50 mol% to 100 mol% of ethylene, based on the total moles of polymerized monomers in the (AP) segment.

15. The composition of any one of claims 10-14, wherein, for the ethylene/vinylarene diblock interpolymer or triblock interpolymer, ≥ 20 mol% of the polymerized vinylarene in each (AR) segment is present in a “back to back” configuration as shown below in subsegment bb:



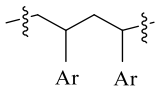
(subsegment bb); and wherein the mol% is based on the total moles of polymerized vinylarene in the (AR) segment.

16. The composition of any one of claims 10-15, wherein, for the ethylene/vinylarene diblock interpolymer or triblock interpolymer, ≥ 20 mol% of the polymerized vinylarene in each (AR) segment is present in a syndiotactic “back to back” configuration as shown below in subsegment sbb:



(subsegment sbb); and wherein the mol% is based on the total moles of polymerized vinylarene in the (AR) segment.

17. The composition of any one of claims 10-16, wherein, for the ethylene/vinylarene diblock interpolymer or triblock interpolymer, none of the polymerized vinylarene in each (AP) segment is present in a “back to back” configuration as shown below in subsegment bb:



(subsegment bb); and wherein the mol% is based on the total moles of polymerized vinylarene in the (AP) segment.

18. The composition of any one of claims 10-17, wherein, for the ethylene/vinylarene diblock interpolymer or triblock interpolymer, the vinylarene is styrene.

19. An article comprising at least one component formed from the composition of any one of claims 10-18.