

DUAL REACTOR CHAIN SHUTTTLING REACTIONS
FOR ETHYLENE/VINYLAARENE DIBLOCK AND TRIBLOCK INTERPOLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of priority to U.S. Provisional Application No. 63/127,350, filed on December 18, 2020, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

The catalytic production of olefin block copolymers (OBC) via chain shuttling technology has resulted in differentiated materials, such as the INFUSE Olefin Block Copolymers and the INTUNE Olefin Block Copolymers. Such copolymers are typically made from ethylene and an alpha-olefin. The use of chain shuttling technology to produce styrenic block interpolymers offers an attractive route to high value polymers using a continuous solution polymerization process. High value styrenic polymers like SEBS (styrene-ethylene/butene-styrene) are produced in a batch process, via anionic polymerization, initiated by organolithium compounds. This costly polymerization consists of the sequential addition of monomers, followed by an expensive hydrogenation step. There is a need for chain shuttling technology to produce ethylene/vinylarene diblock and triblock interpolymers using dual reactor, continuous solution polymerization.

A. Valente et al., *Angew. Chem., Int. Ed.* 2014, 53, 4638-4641, *Isoprene-Styrene Chain Shuttling Copolymerization Mediated by a Lanthanide Half-Sandwich Complex and a Lanthanidocene: Straightforward Access to a New Type of Thermoplastic Elastomers*, discloses an isoprene and styrene chain shuttling polymerization, using with n-butylethylmagnesium, a lanthanide half-sandwich complex and a lanthanidocene. The resulting multiblock structures have alternating hard (styrene-rich) and soft (isoprene-rich) segments.

U.S. Publication 2014/0088276 (*Manufacturing Method for Multidimensional Polymer, and Multidimensional Polymer*) discloses the polymerization of stereo-controlled (syndiotactic) block copolymers of a styrene-type monomer with a conjugated diene, such as isoprene or butadiene, by chain shuttling technology and coordinative chain transfer polymerization. The polymerization takes place in the presence of a first catalyst and a second catalyst. Each of the first catalyst and the second catalyst, independently, contain the following: a) a group 3 metal atom or a lanthanoid metal atom, and for example, Sc, b) a Cp-

type ligand containing a substituted or an unsubstituted cyclopentadienyl derivative, c) monoanion ligands, and d) a neutral Lewis base.

U.S. Patent 8,623,976 (*Polymerization Catalyst Compositions Containing Metallocene Complexes and the Polymers Produced by Using the Same*) discloses a catalyst composition comprising the following: a) metallocene complex containing the following:

- i) a group 3 metal atom or a lanthanoid metal atom, and for example, Sc,
- ii) a Cp* ligand of a substituted or an unsubstituted cyclopentadienyl derivative,
- iii) monoanionic ligand,
- iv) a neutral Lewis base;

b) an ionic compound of a non-ligand anion and a cation, and for example, tetrakis(pentafluorophenyl)borate. The catalyst composition is used to polymerize various polymers, such as ethylene/styrene copolymers (see Examples 11-17). The polymerized styrene may be in syndiotactic form.

L. Pan et al., *Angew. Chem., Int. Ed.* 2011, 50, 12012-12015, *Chain-Shuttling Polymerization at Two Different Scandium Sites: Regio- and Stereospecific "One-Pot" Block Copolymerization of Styrene, Isoprene, and Butadiene*, discloses the chain-shuttling polymerization of styrene, isoprene and butadiene, by two different catalysts and a chain shuttling agent (triisobutylaluminum, TIBA). The catalysts show different monomer selectivity and stereoselectivity in the presence of TIBA, resulting in the regio- and stereospecific copolymerization of styrene, isoprene and butadiene.

S. S. Park et al., *Macromolecules* 2017, 50, 6606-6616, *Biaxial Chain Growth of Polyolefin and Polystyrene from 1,6-Hexanediylzinc Species for Triblock Copolymers*, discloses the preparation of triblock copolymers, by initiating (anionic) styrene polymerization from a polymeryl zincate species. A polyethylene/polypropylene copolymer is grown from a dual-headed zinc species using coordinative chain transfer polymerization, followed by addition of the anionic initiator (for example, Me₃SiCH₂Li-(pmdeta)) and styrene monomer. The coordinative chain transfer polymerization takes place in the presence of a transition metal (for example, Zr or Hf) complex. Thus, anionic polymerization is used to grow polystyrene end blocks, which do not exhibit any stereoregularity.

U.S. Publication 2018/0022852 (*Organic Zinc Compound Comprising Polyolefin-Polystyrene Block Copolymer, and Method for Preparing the Same*) discloses the preparation of an organic zinc compound, such as that of Formula 1, as shown therein, and which comprises a styrene-based polymer or a polyolefin-polystyrene block copolymer. This preparation method comprises preparing an intermediate by coordination polymerizing an

olefin monomer using a transition metal catalyst, and then inserting, in part, styrene monomers into the intermediate by anionic polymerization. Transition metal catalysts include Zr metal compounds represented by Formula 6A and Formula 6B, each shown therein (see paragraphs [0076] and [0077]).

Y. Luo et al., *J. Am. Chem. Soc.* 2004, 126, 13910-13911, *Scandium Half-Metallocene-Catalyzed Syndiospecific Styrene Polymerization and Styrene-Ethylene Copolymerization: Unprecedented Incorporation of Syndiotactic Styrene-Styrene Sequences in Styrene-Ethylene Copolymers*, discloses the polymerization of syndiospecific styrene-ethylene copolymers, using a scandium half-sandwich complex. The melting temperature (T_m) of the copolymer can be modified by adjusting the ethylene incorporation, where ethylene incorporation results in a decrease in the T_m . No chain-shuttling was demonstrated with the Sc catalyst.

H. Hagihara et al., *Polymer Journal* 2012, 44, 147-154, *Synthesis of Ethylene-Styrene Copolymer Containing Syndiotactic Polystyrene Sequence by Trivalent Titanium Catalyst*, discloses the polymerization of syndiotactic styrene-ethylene copolymers, using a trivalent titanium catalyst, tris(acetylacetonate) titanium ($Ti(acac)_3$). Different polymers were produced by the $Ti(acac)_3$ catalyst, which may be attributed to the presence of multiple oxidation sites on this catalyst.

F. Lin et al., *Journal of Polymer Science, Part A: Polymer Chemistry* 2017, 55, 1243-1249, *Synthesis and Characterization of Crystalline Styrene-*b*-(Ethylene-co-Butylene)-*b*-Styrene Triblock Copolymers*, discloses the synthesis and characterization of crystalline styrene-*b*-(ethylene-co-butylene)-*b*-styrene (SEBS). The cationic, rare earth metal complex, $[(\eta^5\text{-Flu-CH}_2\text{-Py})\text{Ho}(\text{CH}_2\text{SiMe}_3)](\text{THF})$, was used for a living polymerization of butadiene and styrene. The sequential addition of styrene, butadiene and styrene monomers formed an SBS triblock. The SBS triblock consisted of elastic polybutadiene sequences with 1,4 regularity and crystalline syndiotactic polystyrene. The SBS triblock was hydrogenated to form the SEBS.

B. Liu et al., *Macromolecules* 2016, 49, 6226-6231, *Regioselective Chain Shuttling Polymerization of Isoprene: An Approach to Access New Materials from Single Monomer*, discloses the chain transfer polymerization of isoprene using a pyridyl-methylene fluorenyl scandium complex, in combination with $[\text{Ph}_3\text{C}]\text{B}(\text{C}_6\text{F}_5)_4$ and $i\text{Bu}_3\text{Al}$. The polymerization yielded high 1,4-selectivity of the isoprene. Additional catalysts structures include "pyridyl-methylene functionalized fluorenyl ligated rare earth metal complexes 1-9, as shown therein, and where the metal is Sc, Y, Lu, Tm, Er, Ho, Dy, Tb or Gd (see page 6227 (Chart 1)).

U.S. Patent 8,710,143 (*Catalyst Composition Comprising Shuttling Agent for Ethylene Multi-Block Copolymer Formation*) discloses the polymerization of multiblock copolymers using the following: (A) a first metal complex olefin polymerization catalyst, (B) a second metal complex olefin polymerization catalyst capable of preparing polymers differing in chemical or physical properties from the polymer prepared by catalyst (A), under equivalent polymerization conditions, and (C) a chain shuttling agent. Suitable monomers include ethylene and one or more addition polymerizable monomers, such as 1-octene and styrene (see column 16, lines 3-32). Suitable catalysts include metal complexes, where the metal is selected from Group 3-15, preferably Groups 3-10, more preferably Groups 4-8, and most preferably Group 4 (Ti, Zr and Hf). See, for example, column 19, line 61, to column 20, line 6. An ethylene/styrene multiblock polymer was prepared using Cat. A1 (Hf) and Cat. B1 (Zr), each as shown therein (see column 85, lines 12-30; column 86, lines 21-52; column 115, line 21, to column 116, line 23 and Tables 27 and 28).

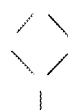
Additional olefin block copolymers (OBCs) and associated polymerizations are disclose in the following references: U.S. Patent 7,915,192; U.S. Patent 8,124,709; U.S. Patent 8,501,885; U.S. Patent 8,716,400; EP1716190B1; EP1926763B1; and EP2582747B1.

However, there remains a need for chain shuttling technology to produce ethylene/stereoregular vinylarene diblock and triblock interpolymers, in dual reactors using continuous solution polymerization. This need has been met by the following invention.

SUMMARY OF THE INVENTION

In a first aspect, 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 (C₁-C₃₀)hydrocarbyl, a substituted or unsubstituted (C₁-C₃₀)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;

R¹ is a bridging group comprising from 2 to 41 atoms other than hydrogen, and wherein, optionally, the bond between R¹ and M is a pi bond;

R² is selected from a substituted or an unsubstituted (C₁-C₃₀)hydrocarbyl group, or a substituted or an unsubstituted (C₁-C₃₀)heterohydrocarbyl group;

J¹ is a bridging group linking N and R¹, 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 (M¹) via an electron donative bond; and

wherein the metal complex is overall charge-neutral;



(Formula S2),

wherein M¹ 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 (C₁-C₃₀)hydrocarbyl, a substituted or unsubstituted (C₁-C₃₀)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 R³ and R⁴ is independently selected from a substituted or an unsubstituted (C₆-C₂₀)aryl group, or a substituted or an unsubstituted (C₅-C₂₀)heteroaryl group;

N and N are linked by a bridging group, J², 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, a substituted or unsubstituted (C_1 - C_{30})heterohydrocarbyl group, $-Si(R^C)_3$, or $-H$;

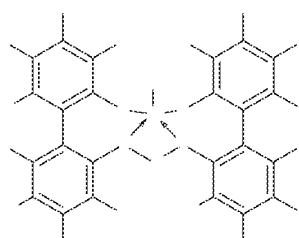
T^1 is selected from $-O-$, $-S-$, $-N(R^N)-$, or $-P(R^P)-$;

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 an unsubstituted (C_1 - C_{30})hydrocarbyl, a substituted or an 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;

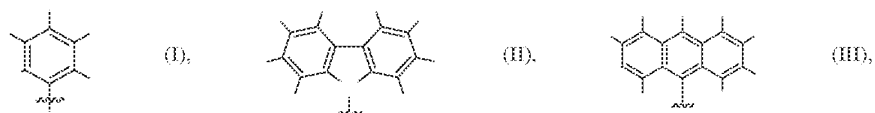
each X is independently selected from a substituted or unsubstituted (C_1 - C_{30})hydrocarbyl, a substituted or unsubstituted (C_1 - C_{30})heterohydrocarbyl, or $-H$; and wherein each X is independently a monodentate ligand or a bidentate ligand;

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

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 - C_{40})hydrocarbyl, a substituted or unsubstituted (C_1 - C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^C S(O)-$,

$R^C S(O)_2-$, $(R^C)_2 C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2 NC(O)-$, halogen, radicals having formula (I), radicals having formula (II), and radicals having formula (III):



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

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

J^4 is a substituted or unsubstituted (C_1-C_{40}) hydrocarbylene or a substituted or unsubstituted (C_1-C_{40}) heterohydrocarbylene, wherein the substituted or unsubstituted (C_1-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 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^{44-51} are each independently selected from a substituted or unsubstituted (C_1 - C_{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^{44-51} 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 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;
 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, X 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.

In a second aspect, a composition comprising an ethylene/vinylarene diblock interpolpolymer or an ethylene/vinylarene triblock interpolpolymer, said diblock interpolpolymer comprising at least one polymer structure selected from Structure 1, as shown below, and said triblock interpolpolymer 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.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is a schematic depicting the formation of an ethylene/styrene diblock interpolpolymer. Each black block represents an vinylarene-poor block comprising, in polymerized form, ethylene, optionally an alpha-olefin and optionally a vinylarene. Each grey (pink) block represents an vinylarene-rich block comprising, in polymerized form, ethylene, a vinylarene and optionally an alpha-olefin.

Figure 1B is a schematic depicting the formation of an ethylene/styrene triblock interpolpolymer. See above for block descriptions.

Figure 2 depicts the ¹H NMR profile of CAT B.

Figure 3 depicts the ¹³C NMR profile of CAT B.

Figure 4 depicts PPR Data: Activity vs CSA Loading (μmoles).

Figure 5 depicts PPR Data: PS Molecule Weight (Mw) vs CSA Loading (μmoles).

Figure 6 depicts conventional GPC profiles of syndiotactic polystyrenes as noted. GPC profiles from left to right, starting at Log M = 3.00: “sPS 3 (100 DEZ polymer),” “sPS-

5 (100 TEA polymer),” “sPS-2 (25 DEZ polymer),” “sPS-4 (25 TEA polymer),” “sPS-1 (no CSA polymer).”

Figure 7 depicts the ¹H NMR profile of Triblock 2 (composition containing an ethylene/octene/styrene triblock).

Figure 8 depicts the ¹³C NMR profile of Triblock 2.

Figure 9 depicts the GPC profile of Triblock 1 (composition containing an ethylene/octene/styrene triblock). A dRI/UV dual detectors were used. GPC profiles from left to right, starting at Log M = 4.00: UV profile, RI profile.

Figure 10A depicts the conventional GPC profiles of the samples as noted. GPC profiles from left to right, starting at Log M = 3.00: Triblock 2, IB-1 (In-Reactor Blend) (see Table 9).

Figure 10B depicts the conventional GPC profiles of the samples as noted. GPC profiles from left to right, starting at Log M = 2.00: IB-2 (In-Reactor Blend), Triblock 3 (composition containing an ethylene/octene/styrene triblock), Diblock 1 (composition containing an ethylene/octene/styrene diblock), Diblock 2 (composition containing an ethylene/octene/styrene diblock) (see Table 7).

Figure 11 depicts Tensile Stress versus Tensile Strain for Triblock 2 and IB-1.

Figure 12 depicts conventional GPC profiles of atactic polystyrenes as noted. GPC profiles from left to right, starting at Log M = 2.00: “aPS-4 (100 DEZ polymer),” “aPS-5 (25 TEA) polymer),” “aPS-3 (25 DEZ polymer),” “aPS-1 (CAT C only polymer),” “aPS-2 (no CSA C and no CSA polymer).”

Figure 13 depicts CAT D PPR Data: Molecular Weight (Mw) versus Polymerization Efficiency.

Figure 14 depicts CAT E PPR Data: Molecular Weight (Mw) versus Polymerization Efficiency.

Figure 15 depicts CAT F PPR Data: Molecular Weight (Mw) versus Polymerization Efficiency.

DETAILED DRESCRIPTION OF THE INVENTION

Chain shuttling technology has been discovered to produce ethylene/vinylarene diblock and triblock interpolymers, via dual catalysts in two reactors. For example, the catalyst (metal complex) used to form vinylarene-poor segments (or blocks) in one reactor meets the following criteria: a) high native molecular weight. b) high chain shuttling constants, as determined by molecular weight reduction and narrowing of the molecular

weight distribution in the presence of CSA (chain shuttling agent), and 3) high α -olefin incorporation. The catalyst (metal complex) used for form vinylarene-rich segments (or blocks) in the other reactor meets the following criteria: a) good activity toward the vinylarene polymerization, b) high chain shuttling constants, as determined by molecular weight reduction and narrowing of the molecular weight distribution in the presence of a CSA, and c) compatibility with residual monomer carried over.

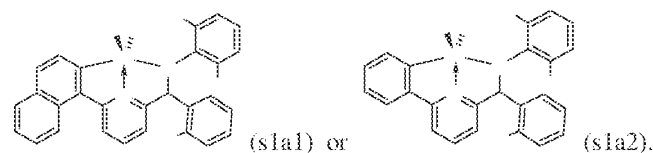
As discussed above, the invention provides, in a first aspect, a process to form a composition comprising an ethylene/vinylarene diblock interpolpolymer and/or an ethylene/vinylarene triblock interpolpolymer, as described above. An inventive process may comprise a combination of two or more embodiments, as described herein. Each step or component of an inventive process may comprise a combination of two or more embodiments, each described herein.

As discussed above, the invention also provides, in a second aspect, a composition comprising an ethylene/vinylarene diblock interpolpolymer or an ethylene/vinylarene triblock interpolpolymer, as described above. An inventive composition may comprise a combination of two or more embodiments, as described herein. The diblock interpolpolymer and the triblock interpolpolymer may each comprise a combination of two or more embodiments, as described herein.

Note, as used herein, in reference to structures of a metal complex, $Ar1 = Ar^1$, $Ar2 = Ar^2$, $Ar3 = Ar^3$, and so forth. Also, as used herein, in reference to such structures, $R1 = R^1$, $R2 = R^2$, $R3 = R^3$, and so forth. The notation R^a-R^n where "a through n" represents consecutive numbers, refers to R^a , R^{a+1} , R^{a+2} , ..., R^n . For example, R^3-R^7 refers to R^3 , R^4 , R^5 , R^6 , R^7 . As used herein, in reference to noted metal complexes, the notation " $\longrightarrow$ " refers to a bond formed from a donating electron pair (electron donative bond). Note, a pi (π) bond is shown herein by a straight line.

The following embodiments apply to an inventive process and/or an inventive composition as applicable.

In one embodiment, or a combination of two or more embodiments, each described herein, the metal complex S is selected from structure s1a1 or structure s1a2:



In one embodiment, or a combination of two or more embodiments, each described herein, metal complex S is selected from Formula S1, and further Formula S1a as described herein; and the metal complex H is selected from Formula H1, and further Formula H1a or Formula H1b, each as described herein.

In one embodiment, or a combination of two or more embodiments, each described herein, the metal complex H is selected from the following formulas h1a1, h1a2, h1a3, h1b1, h1b2, h1b3, h2a1 or h2a2, each as described herein.

In one embodiment, or a combination of two or more embodiments, each described herein, 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.

In one embodiment, or a combination of two or more embodiments, each described herein, step A occurs before step B.

In one embodiment, or a combination of two or more embodiments, each described herein, step B occurs before step A.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, the vinylarene is styrene.

In one embodiment, or a combination of two or more embodiments, each described herein, the mixture A comprises the alpha-olefin.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≥ 15 mol%, or ≥ 20 mol%, or ≥ 25 mol%, or ≥ 30 mol%, or ≥ 35 mol%, or ≥ 40 mol%, or ≥ 45 mol%, or ≥ 50 mol%, or ≥ 55 mol%, or ≥ 60 mol%, of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment. In one embodiment, or a combination of two or more embodiments, each described herein, each (AR) segment independently comprises, in polymerized form, < 100 mol%, or ≤ 98 mol%, or ≤ 96 mol%, or ≤ 94 mol%, or ≤ 92 mol%, or ≤ 91 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≥ 0 mol%, or ≥ 0.2 mol%, or ≥ 0.4 mol%, or ≥ 0.6 mol%, or ≥ 0.8 mol%, or ≥ 1.0 mol% of the

vinylarene, based on the total moles of polymerized monomers in the (AP) segment. In one embodiment, or a combination of two or more embodiments, each described herein, each (AP) segment independently comprises, in polymerized form, ≤ 10 mol%, or ≤ 9.0 mol%, or ≤ 8.0 mol%, or ≤ 7.0 mol%, or ≤ 6.0 mol%, or ≤ 5.0 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AP) segment.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≥ 2.0 mol%, or ≥ 4.0 mol%, or ≥ 6.0 mol%, or ≥ 8.0 mol%, or ≥ 9.0 mol%, or ≥ 10 mol%, or ≥ 11 mol%, or ≥ 12 mol%, or ≥ 13 mol%, or ≥ 14 mol% of ethylene, based on the total moles of polymerized monomers in the (AR) segment. In one embodiment, or a combination of two or more embodiments, each described herein, each (AR) segment independently comprises, in polymerized form, ≤ 80 mol%, or ≤ 77 mol%, or ≤ 75 mol%, or ≤ 73 mol%, or ≤ 70 mol%, or ≤ 65 mol%, or ≤ 60 mol%, or ≤ 55 mol%, or ≤ 50 mol%, or ≤ 45 mol%, or ≤ 40 mol% of ethylene, based on the total moles of polymerized monomers in the (AR) segment.

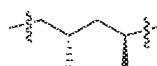
In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form ≥ 50 mol%, ≥ 52 mol%, or ≥ 54 mol%, or ≥ 56 mol%, or ≥ 58 mol%, or ≥ 60 mol%, or ≥ 62 mol%, or ≥ 64 mol%, or ≥ 66 mol%, or ≥ 68 mol%, or ≥ 70 mol% of ethylene, based on the total moles of polymerized monomers in the (AP) segment. In one embodiment, or a combination of two or more embodiments, each described herein, each (AP) segment independently comprises, in polymerized form, ≤ 100 mol%, or ≤ 98 mol%, or ≤ 96 mol%, or ≤ 94 mol%, or ≤ 92 mol%, or ≤ 90 mol% of ethylene, based on the total moles of polymerized monomers in the (AP) segment.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≥ 20 mol%, or ≥ 40 mol%, or ≥ 60 mol%, or ≥ 80 mol%, or ≥ 85 mol%, or ≥ 90 mol%, or ≥ 92 mol%, or ≥ 94 mol%, or ≥ 96 mol%, or ≥ 98 mol%, or ≥ 99 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.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≥ 20 mol%, or ≥ 40 mol%, or ≥ 60 mol%, or ≥ 80 mol%, or ≥ 85 mol%, or ≥ 90 mol%, or ≥ 92 mol%, or ≥ 94 mol%, or ≥ 96 mol%, or ≥ 98 mol%, or ≥ 99 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.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, none of the polymerized vinylarene in each (AP) segment is present in a "back to back" configuration as shown in subsegment bb:



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

Also provided is a composition formed from an inventive process as described herein. Also provided is an article comprising at least one component formed from an inventive composition.

Ethylene/Vinylarene Diblock and Triblock Interpolymers

Examples of the formation of an ethylene/vinylarene diblock interpolpolymer and the formation of an ethylene/vinylarene triblock interpolpolymers are schematically shown in Figure 1A and Figure 1B, respectively. According to these figures, an ethylene/alpha-olefin random copolymer "block," directly bound to an organometallic reagent, such as a zinc or aluminum-based chain-shuttling agent (CSA) or a dual-headed chain shuttling agent (DHCSA), is generated in the first reactor, using a first transition metal catalyst. These resulting polymeryl zinc or polymeryl aluminum species of the first reactor are transferred into the second reactor. The lifetime of the first transition metal catalyst (metal complex) is spent by the time the contents of the first reactor are transferred to the second reactor. In the second reactor,

styrene, ethylene and optionally, the alpha-olefin, are polymerized in the presence of a second transition metal catalyst, to produce a random styrene/ethylene interpolymers "block." The polymeryl zinc or polymeryl aluminum species from first reactor then undergoes chain shuttling with the second reactor catalyst, to grow the styrene/ethylene random "block" onto the ethylene/alpha-olefin polymeryl chain, yielding the desired diblock (Figure 1A) or triblock (Figure 1B) interpolymers. The two types of random blocks (vinylarene-rich or hard block and vinylarene-poor or soft block) differ in chemical or physical properties. Each block has two or more monomer types that are substantially randomly distributed within the block.

As discussed, the ethylene/vinylarene diblock and triblock interpolymers comprise two chemically distinct regions (referred to as "blocks"), preferably joined in a linear manner. In an embodiment, the blocks differ in the amount or type of incorporated comonomer, density, amount of crystallinity, type or degree of tacticity (isotactic or syndiotactic), or any other chemical or physical property. Compared to conventional block interpolymers of the art, including interpolymers produced by sequential monomer addition, fluxional catalysts, or anionic polymerization techniques, the present ethylene/vinylarene diblock and triblock interpolymers are characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn or MWD), block length distribution, and/or block number distribution, due to the effect of the shuttling agent(s) in combination with multiple catalysts, used in their preparation in dual reactors.

Vinylarene Monomers

Vinylarene monomers are aromatic monomers, and include, but are not limited to, aromatic vinyl compounds such as mono- or poly-alkylstyrenes (including styrene, *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, *o,p*-dimethylstyrene, *o*-ethylstyrene, *m*-ethylstyrene and *p*-ethylstyrene), and functional group-containing derivatives, such as, *o*-chlorostyrene, *m*-chlorostyrene, *p*-chlorostyrene, divinylbenzene, 3-phenylpropene, 4-phenylpropene and α -methylstyrene, provided the monomer is polymerizable under the conditions employed.

Chain shuttling agent (CSA)

The term, "chain shuttling agent (CSA)" refers to a compound or a mixture of compounds that is capable of causing a polymeryl exchange between at least two active catalyst sites of the catalysts included in the conditions of the polymerization. That is, transfer of a polymer fragment occurs both to, and from, one or more of the active catalyst

sites. The CSA is able to chain transfer between, for example, the "AP (soft block) catalyst" and the "AR (hard block catalyst)."

Suitable shuttling agents include, but are not limited to, Group 1, 2, 12 or 13 metal compounds or complexes containing at least one substituted or unsubstituted hydrocarbyl group, preferably hydrocarbyl substituted aluminum, gallium or zinc compounds containing from 1 to 12 carbons in each hydrocarbyl group, and reaction products thereof with a proton source. Preferred hydrocarbyl groups are alkyl groups, preferably linear or branched, C2-C8 alkyl groups. Chain shuttling agents include, but are not limited to, trialkylaluminum and dialkyl zinc compounds, especially triethylaluminum, tri(isopropyl)aluminum, tri(isobutyl)aluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum, triethylgallium, or diethylzinc. See U.S. Patent 8,710,143 (incorporated herein by reference).

Dual-headed chain shuttling agents (for example, an Al-DHCSA and an AlZn-DHCSA) are also suitable agents. Dual-headed chain shuttling agents include, but are not limited to structures of the following formula: $R1-[M-R2-]_n-M-R1$ where R1, R2 are each independently a hydrocarbon containing between 1 and 20 carbons, $n \geq 1$, and $M = Zn$. See also WO2018/064546 and U.S. Patent 8,501,885 (each incorporated herein by reference).

DEFINITIONS

Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percentages are based on weight, and all test methods are current as of the filing date of this disclosure.

The term "composition," as used herein, includes a mixture of materials, which comprise the composition, as well as reaction byproducts and decomposition products formed from the materials of the composition. Any reaction byproduct or decomposition product is typically present in trace or residual amounts.

The term "polymer," as used herein, refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus includes the term homopolymer (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term interpolymer as defined hereinafter. Trace amounts of impurities, such as catalyst residues, can be incorporated into and/or within the polymer. Typically, a polymer is stabilized with very low amounts ("ppm" amounts) of one or more stabilizers.

The term "interpolymer," as used herein, refers to a polymer prepared by the polymerization of at least two different types of monomers. The term interpolymer thus includes the term copolymer (employed to refer to polymers prepared from two different types of monomers) and polymers prepared from more than two different types of monomers.

The term "olefin-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, 50 wt% or a majority weight percent of an olefin, such as ethylene or propylene (based on the weight of the polymer), and optionally may comprise one or more comonomers.

The term "propylene-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, a majority weight percent of propylene (based on the weight of the polymer), and optionally may comprise one or more comonomers.

The term "ethylene-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, 50 wt% or a majority weight percent of ethylene (based on the weight of the polymer), and optionally may comprise one or more comonomers.

The term "vinylarene-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, a majority weight percent of the vinylarene (based on the weight of the polymer), and optionally may comprise one or more comonomers.

The term "styrene-based polymer," as used herein, refers to a polymer that comprises, in polymerized form, a majority weight percent of styrene (based on the weight of the polymer), and optionally may comprise one or more comonomers.

The term "ethylene/alpha-olefin interpolymer," as used herein, refers to a random interpolymer that comprises, in polymerized form, 50 wt% or a majority weight percent of ethylene (based on the weight of the interpolymer), and an alpha-olefin.

The term, "ethylene/alpha-olefin copolymer," as used herein, refers to a random copolymer that comprises, in polymerized form, 50 wt% or a majority weight percent of ethylene (based on the weight of the copolymer), and an alpha-olefin, as the only two monomer types.

The term, "ethylene/vinylarene copolymer," as used herein, refers to a random copolymer that comprises, in polymerized form, 50 wt% or a majority weight percent of ethylene (based on the weight of the copolymer), and a vinylarene, as the only two monomer types.

The phrase "a majority weight percent," as used herein, in reference to a polymer (or interpolymer, or terpolymer or copolymer), refers to the amount of monomer present in the greatest amount in the polymer.

The term "ethylene/vinylarene diblock interpolymers," as used herein, refers to a diblock interpolymers that comprises a vinylarene-rich (AR) segment and a vinylarene-poor (AP) segment. See, for example, Figure 1A. The AR segment comprises, in polymerized form, > 10 mol% of the vinylarene. The AP segment comprises, in polymerized form, ≤ 10 mol% of the vinylarene. Each mol% is based on the total moles of polymerized monomers in the respective segment. The diblock interpolymers comprises, in polymerized form, ethylene, the vinylarene, and may comprises other monomer types. The term "ethylene/vinylarene diblock copolymer," as used herein, refers to a diblock copolymer that comprises a vinylarene-rich (AR) segment, as discussed above, and a vinylarene-poor (AP) segment, as discussed above. The diblock copolymer comprises, in polymerized form, ethylene and the vinylarene, as the only two monomer types.

The term "ethylene/alpha-olefin/vinylarene diblock interpolymers," as used herein, refers to a diblock interpolymers that comprises a vinylarene-rich (AR) segment and a vinylarene-poor (AP) segment. See, for example, Figure 1A. The AR segment comprises, in polymerized form, > 10 mol% of the vinylarene. The AP segment comprises, in polymerized form, ≤ 10 mol% of the vinylarene. Each mol% is based on the total moles of polymerized monomers in the respective segment. The diblock interpolymers comprises, in polymerized form, ethylene, the alpha-olefin and the vinylarene, and may comprises other monomer types. The term "ethylene/alpha-olefin/vinylarene diblock terpolymer," as used herein, refers to a diblock terpolymer that comprises a vinylarene-rich (AR) segment, as discussed above, and a vinylarene-poor (AP) segment, as discussed above. The diblock terpolymer comprises, in polymerized form, ethylene, the alpha-olefin, the vinylarene, as the only three monomer types.

The term "ethylene/vinylarene triblock interpolymers," as used herein, refers to a triblock interpolymers that comprises either two vinylarene-rich (AR) segments and one vinylarene-poor (AP) segment located between the AR segments, or two vinylarene-poor (AP) segments and one vinylarene-rich (AR) segment, located between the AP segments. See, for example, Figure 1B. The AR segment comprises, in polymerized form, > 10 mol% of the vinylarene. The AP segment comprises, in polymerized form, ≤ 10 mol% of the vinylarene. Each mol% is based on the total moles of polymerized monomers in the respective segment. The triblock interpolymers comprises, in polymerized form, ethylene, the vinylarene, and may comprises other monomer types. The term "ethylene/vinylarene triblock copolymer," as used herein, refers to a triblock copolymer that comprises either two vinylarene-rich (AR) segments and one vinylarene-poor (AP) segment, as discussed above, or

two vinylarene-poor (AP) segments and one vinylarene-rich (AR) segment, as discussed above. Each AR segment and AP segment are described above. The triblock copolymer comprises, in polymerized form, ethylene and the vinylarene, as the only two monomer types.

The term "ethylene/alpha-olefin/vinylarene triblock interpolmer," as used herein, refers to a triblock interpolmer that comprises either two vinylarene-rich (AR) segments and one vinylarene-poor (AP) segment, located between the AR segments, or two vinylarene-poor (AP) segments and one vinylarene-rich (AR) segment, located between the AP segments. See, for example, Figure 1B. The AR segment comprises, in polymerized form, > 10 mol% of the vinylarene. The AP segment comprises, in polymerized form, ≤ 10 mol% of the vinylarene. Each mol% is based on the total moles of polymerized monomers in the respective segment. The triblock interpolmer comprises, in polymerized form, ethylene, the alpha-olefin, the vinylarene, and may comprises other monomer types. The term "ethylene/alpha-olefin/vinylarene triblock terpolymer," as used herein, refers to a triblock terpolymer that comprises, in polymerized form, either two vinylarene-rich (AR) segments and one vinylarene-poor (AP) segment, as discussed above, or two vinylarene-poor (AP) segments and one vinylarene-rich (AR) segment, as discussed above. Each AR segment and AP segment are described above. The triblock terpolymer comprises, in polymerized form, ethylene, the alpha-olefin and the vinylarene, as the only three monomer types.

The term "vinylarene," as used herein, refers to a chemical compound comprising a " $-\text{CR}=\text{CHR}'$ " (where R and R' are each independently H or an alkyl)" bonded to an aromatic ring structure, such as a monocyclic, bicyclic or tricyclic ring structure. The aromatic ring structure may or may not comprise one or more heteroatom groups, and may or may not be substituted with one or more heteroatom groups. Examples of vinylarenes include, but are not limited to, styrene, 2-vinyl toluene and 4-vinyltoluene, and alpha-methyl styrene.

The term "alkylsilane group," as used herein, refers to a chemical group comprising at least on $-\text{Si}-\text{R}$ moiety, where R is an alkyl. Some examples of such groups include the following: $-\text{CH}_2-\text{Si}(\text{CH}_3)_3$, $-\text{CH}_2-\text{Si}(\text{H})(\text{CH}_3)_2$, $-\text{CH}_2-\text{Si}(\text{H})_2(\text{CH}_3)$, $-\text{Si}(\text{CH}_3)_3$, $-\text{Si}(\text{H})(\text{CH}_3)_2$, $-\text{Si}(\text{H})_2(\text{CH}_3)$.

The term "heteroatom," refers to an atom other than hydrogen or carbon (for example, O, N or P).

The term "heteroatom group" refers to a heteroatom or to a chemical group containing one or more heteroatoms.

The terms “hydrocarbon,” “hydrocarbyl group,” and similar terms, as used herein, refer to a respective compound or chemical group, etc., containing only carbon and hydrogen atoms. A divalent “hydrocarbylene group” is defined in similar manner.

The terms “heterohydrocarbon,” “heterohydrocarbyl group,” and similar terms, as used herein, refer to a respective hydrocarbon,” or “hydrocarbyl group, etc., in which at least one carbon atom is substituted with a heteroatom group (for example, O, N or P). The monovalent heterohydrocarbyl group may be bonded to the remaining compound of interest via a carbon atom or via a heteroatom. A divalent “heterohydrocarbylene group” is defined in similar manner; and the divalent heterohydrocarbylene group may be bonded to the remaining compound of interest via two carbon atoms, or two heteroatoms, or a carbon atom and a heteroatom.

The terms “substituted hydrocarbon,” “substituted hydrocarbyl group,” and similar terms, as used herein, refer to a respective hydrocarbon or hydrocarbyl group, etc., in which one or more hydrogen atoms is/are independently substituted with a heteroatom group.

The terms “substituted heterohydrocarbon,” “substituted heterohydrocarbyl group,” and similar terms, as used herein, refer to a respective heterohydrocarbon or heterohydrocarbyl group, etc., in which one or more hydrogen atoms is/are independently substituted with a heteroatom group.

The term “aryl,” “aryl group,” and similar terms used herein, refer to a monovalent aromatic hydrocarbyl or aromatic hydrocarbyl group, etc., comprising one or more ring structures; for example, a monocyclic, a bicyclic or a tricyclic ring structure.

The term “heteroaryl,” “heteroaryl group,” and similar terms used herein, refer to a monovalent aryl or aryl group, etc., in which one or more carbon atoms of the backbone ring structure(s) is/are independently replaced with a heteroatom group.

The terms “substituted aryl,” “substituted aryl group,” and similar terms, as used herein, refer to an aryl or aryl group, etc., in which one or more hydrogen atoms is/are independently substituted with a heteroatom group.

The terms “substituted heteroaryl,” “substituted heteroaryl group,” and similar terms, as used herein, refer to a heteroaryl or heteroaryl group, etc., in which one or more hydrogen atoms is/are independently substituted with a heteroatom group.

The term “arylene,” “arylene group,” and similar terms used herein, refer to a divalent aromatic hydrocarbylene or aromatic hydrocarbylene group, etc., comprising one or more ring structures; for example, a monocyclic, a bicyclic or a tricyclic ring structure.

The terms “substituted arylene,” “substituted arylene group,” and similar terms, as used herein, refer to an arylene or arylene group, etc., in which one or more hydrogen atoms is/are independently substituted with a heteroatom group.

The term “substituted or unsubstituted (C₁–C₃₀)hydrocarbonyl,” and other like terms, as used herein, denoted the range of total carbon atoms (for example, 1 to 30) that a substituted or unsubstituted hydrocarbonyl radical may contain. Note, other monovalent chemical groups (for example, a substituted or unsubstituted (C₆–C₂₀) aryl group) with a noted carbon range are defined in like manner.

The term “substituted or unsubstituted (C₁–C₃₀)heterohydrocarbonyl,” and other like terms, as used herein, denoted the range of total carbon atoms (for example, 1 to 30) that a “substituted or unsubstituted heterohydrocarbonyl radical may contain. Note, other monovalent chemical groups with a noted carbon range are defined in like manner.

The term “substituted or unsubstituted (C₆–C₂₀) arylene group,” and other like terms, as used herein, denote the range of total carbon atoms (for example 2 to 6) that a substituted or unsubstituted arylene group may contain. Note, other divalent chemical groups with a noted carbon range are defined in like manner.

The term “bridging group,” as used herein, in reference to a metal complex, refers to a divalent organic group that is bonded to two atoms, located at different points in the remaining structure of the metal complex. For example, see the bridging groups of each of Formulas S1 (J¹), S2 (J²), S3 (J³), S4 (J⁴), S5 (J⁵), H2 (J⁵).

The phrase “bridging group comprising from 2 to 40 atoms other than hydrogen,” and similar phrases, as used herein, in reference to a metal complex, denote the range of total atoms other than hydrogen (for example 2 to 40) that an bridging group may contain. Note, other bridging groups with a noted carbon range are defined in like manner.

The term “Lewis base,” as used herein, in reference to a metal complex, refers to a chemical compound or chemical group that can donate a pair of electrons to form a bond with a metal or another chemical group. Examples of Lewis bases include, but are not limited to, tetrahydrofuran (THF), diethylether, dimethylaniline, or trimethylphosphine.

The terms “syndiotacticity,” “syndiotactic,” and similar terms, as used herein, in reference to polymerized vinylarene units, refer to an alternating stereochemical configuration of two or more pendant aryl (for example, phenyl) groups. See for example, subsegment sbb.

The term “polymer structure,” in reference to Structures 1, 2 and 3, refers to the entire molecule of the noted ethylene/vinylarene diblock interpolpolymer or ethylene/vinylarene triblock interpolpolymer.

The notation “AR,” in reference to a diblock or triblock interpolpolymer, refer to a polymer segment of the respective interpolpolymer that comprises, in polymerize form, > 10 mol% of a vinylarene. This notation refers to a “vinylarene-rich” segment.

The notation “AP,” in reference to a diblock or triblock interpolpolymer, refer to a polymer segment of the respective interpolpolymer that comprises, in polymerize form, ≤ 10 mol% of a vinylarene. This notation refers to a “vinylarene-poor” segment.

The phrase “each segment,” in reference to an AR segment (or block) or an AP segment (or block), refers to an AR segment or an AP segment located at the end of the polymer molecule or within the polymer molecule. In reference to a diblock interpolpolymer, an AR segment is located at one end of a polymer molecule, and an AP segment is located at the other end of the polymer molecule. In reference to a triblock interpolpolymer, two AR segments are located at each end of a polymer molecule and an AP segment is located between these two AR segments, or two AP segments are located at each end of a polymer molecule and an AR segment is located between these two AP segments.

The term “solution polymerization,” as used herein, refers to a polymerization process in which the monomer(s), catalyst(s) and formed polymer are all soluble in the polymerization solvent or solvent blend of two or more solvents.

The term “continuous solution polymerization,” as used herein, refers to a solution polymerization in which monomer(s) are continually fed to a reactor, and polymer is continually removed from the reactor.

The term “metal complex,” as used herein, refers to a chemical structure comprising a metal or metal ion that is bonded and/or coordinated to one or more ligands (ions or molecules that contain one or more pairs of electrons that can be shared with the metal). See for example, the metal complexes of Formulas S1, S2, S3, S4, S5, H1 and H2. The metal complex is typically rendered catalytically active by the use of one or more cocatalysts.

The term “scavenger,” as used herein, refers to a chemical compound added to a polymerization reaction to remove or deactivate impurities or unwanted reaction products (for example, oxygen). Examples of some scavenger include aluminum alkyl compounds, such as MMAO and MMAO-3A.

The term “reactor product,” as used herein, refers to the final polymerization mixture in a reactor, and which comprises one or more polymer(s), and typically solvent,

The terms "comprising," "including," "having," and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step or procedure, not specifically delineated or listed.

Listing of Some Processes and Compositions

A) A process to form a composition comprising an ethylene/vinylarene diblock interpolpolymer and/or an ethylene/vinylarene triblock interpolpolymer, and further ethylene/vinylarene diblock interpolpolymer or an ethylene/vinylarene triblock interpolpolymer, 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:



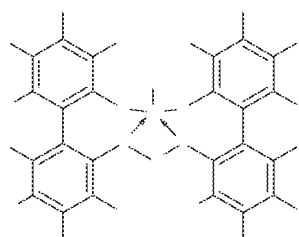
(Formula S1), as described above (see Summary of the Invention (SOI));



(Formula S2), as described above (see SOI); and with respect to 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; further each of R^3 and R^4 is independently selected from a substituted or an unsubstituted (C_6 - C_{12})aryl group, or a substituted or an unsubstituted (C_5 - C_{11})heteroaryl group;



(Formula S3), as described above (see SOI);



(Formula S4), as described above (see SOI);



(Formula S5), as described above (see SOI);

B) polymerizing in a reactor B, a mixture B comprising ethylene, a vinylarene, and optionally an α -olefin, in the presence of at least the following:

wherein the metal complex is overall charge-neutral; or

b) a metal complex H selected from the following Formula H1 or Formula H2:



(Formula H1), as described above (see SOI);

(Formula H2), as described above (see SOI); and with respect to 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; further R^1 and R^2 each independently may be an arylene group (unsubstituted);

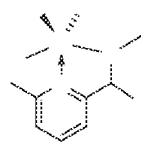
wherein step A occurs before step B, and at least a portion, and further ≥ 50 wt%, or ≥ 80 wt%, or ≥ 90 wt%, or ≥ 98 wt%, of the reactor product in reactor A is transferred to reactor B; or step B occurs before step A, and at least a portion, and further ≥ 50 wt%, or ≥ 80 wt%, or ≥ 90 wt%, or ≥ 98 wt%, of the reactor product in reactor B is transferred to reactor A; and wherein each wt% is based on the total weight of the respective reactor product; 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.

B] The process of A] above, wherein, the metal complex S is selected from the following: Formula S1a or Formula S2a:



(Formula S1a),

wherein X^1 and X^2 are each independently selected from a substituted or unsubstituted (C_1-C_{30}) hydrocarbyl, a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl, or $-H$, and further a substituted or unsubstituted benzyl, or $-H$; and wherein X^1 and X^2 may optionally be linked;

Ar^1 and Ar^2 are each, independently, a substituted or unsubstituted aryl or a substituted or unsubstituted heteroaryl group,

R^{S2} is a substituted or unsubstituted arylene group;



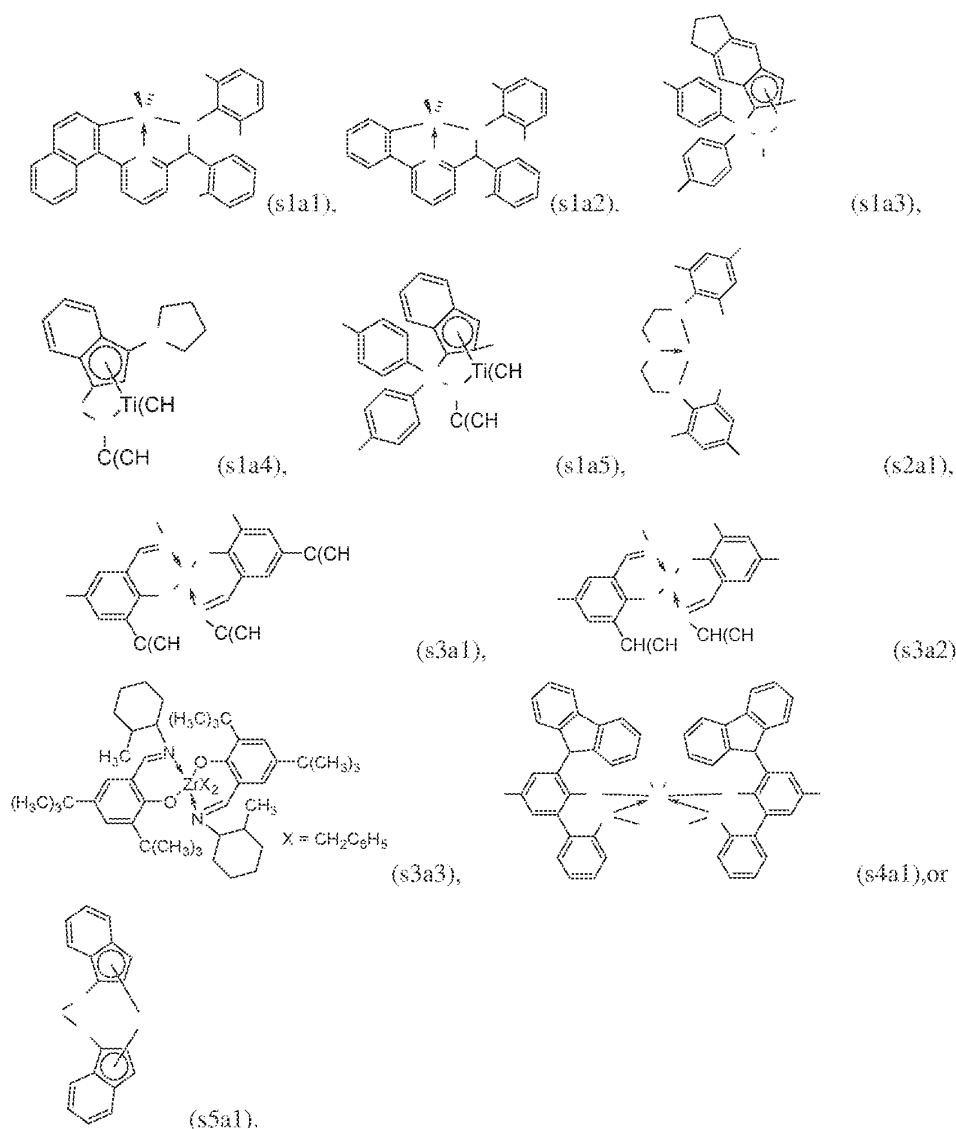
(Formula S2a),

wherein X^3 and X^4 are each independently selected from a substituted or unsubstituted (C_1-C_{30}) hydrocarbyl, a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl, or $-H$, and further a substituted or unsubstituted benzyl, or $-H$; and wherein X^3 and X^4 may optionally be linked;

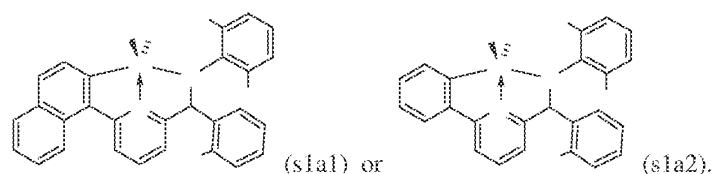
R^{53} is selected from a substituted or unsubstituted (C_1 - C_{30})hydrocarbyl, a substituted or unsubstituted (C_1 - C_{30})heterohydrocarbyl, or $-H$, and further a substituted or unsubstituted benzyl, or $-H$.

Ar^3 and Ar^4 are each, independently, a substituted or unsubstituted aryl or a substituted or unsubstituted heteroaryl group.

C] The process of A] or B] above, wherein, metal complex S selected from the following structures: s1a1, s1a2, s1a3, s1a4, s1a5, s2a1, s3a1, s3a2, s3a3, s4a1 or s5a1, and further any combination of two or more of these structures:



D] The process of any one of A]-C] (A] through C]) above, wherein, the metal complex S is selected from structure s1a1 or structure s1a2:



E] The process of A]-D] above, wherein, the metal complex H is selected from the following: Formula H1a, Formula H1b, or Formula H2a:



(Formula H1a), wherein R^1 , R^2 , R^3 , R^4 , and R^5 are each independently

H, a substituted or unsubstituted hydrocarbyl group, a substituted or unsubstituted heterohydrocarbyl group; and further H, an alkyl group or an alkylsilyl group; and further an alkyl group or an alkylsilyl group;

Q^1 and Q^2 are each independently a substituted or unsubstituted hydrocarbyl group; a substituted or unsubstituted heterohydrocarbyl group; or a halogen; and further an aryl group; an alkylsilyl group, an alkoxy group, a halogen, or $-NRR'$, wherein R and R' are each independently a hydrocarbyl or an SiR'' , where R'' is an hydrocarbyl; and further an aryl group, an alkylsilyl group or an alkoxy group; and

L is a Lewis base, each n is independently 0 or 1; 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;



(Formula H1b), wherein R^1 , R^2 , R^3 , R^4 , and R^5 are each independently

H, a substituted or unsubstituted hydrocarbyl group, or a substituted or unsubstituted heterohydrocarbyl group; and further H an alkyl group or an alkylsilyl group, and further an alkyl group or an alkylsilyl 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; and further an aryl group; an alkylsilyl group, an alkoxy group, a halogen, or $-NRR'$, wherein R and R' are

each independently a hydrocarbyl or an SiR^{''}, where R^{''} is an hydrocarbyl; and further an aryl group, an alkoxy group or a halogen; and

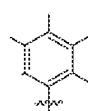
wherein optionally at least one R group and at least one Q group are connected;



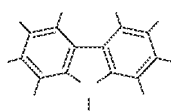
(Formula H2a), wherein M² is Ti, Hf, or Zr, and further Zr or Hf, and

further Zr; and wherein;

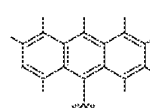
R⁶ and R⁸ are each independently selected from the group consisting of -H, a substituted or unsubstituted (C₁-C₄₀)hydrocarbyl, a substituted or unsubstituted (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R)-, (R^C)₂NC(O)-, halogen, radicals having formula (I), radicals having formula (II), and radicals having formula (III):



(I),



(II),



(III),

where each of R³¹⁻³⁵, R⁴¹⁻⁴⁸, and R⁵¹⁻⁵⁹ is independently selected from a substituted or unsubstituted (C₁-C₄₀)hydrocarbyl, a substituted or unsubstituted (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -N=CHR^C, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, halogen, or -H;

each of R⁷ and R⁹ is independently selected from a substituted or unsubstituted (C₁-C₄₀)hydrocarbyl, a substituted or unsubstituted (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -N=CHR^C, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, halogen, or -H;

R¹⁰ is optional, and if present is a substituted or unsubstituted (C₁-C₄₀)hydrocarbylene or a substituted or unsubstituted (C₁-C₄₀)heterohydrocarbylene;

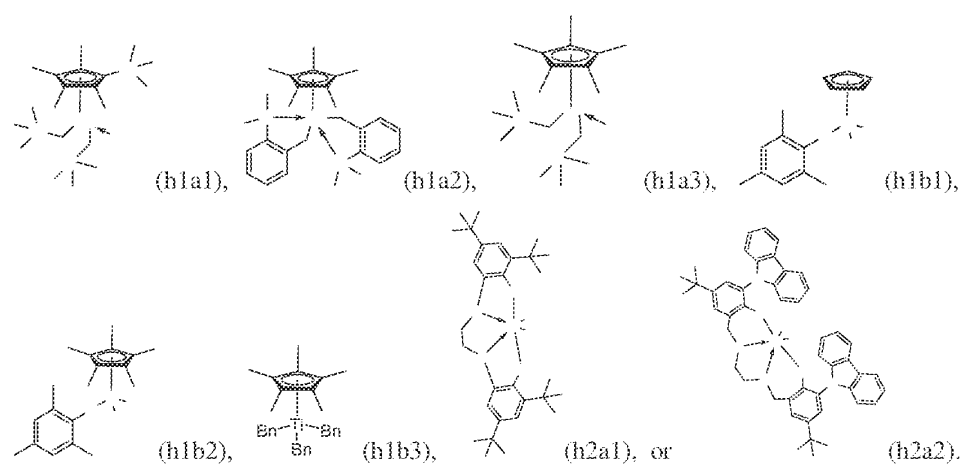
R^{11} is optional, and if present is a substituted or unsubstituted (C_1-C_{40}) hydrocarbylene or a substituted or unsubstituted (C_1-C_{40}) heterohydrocarbylene;

Q1 and Q2 are each independently a substituted or unsubstituted hydrocarbyl group or a halogen, and further an aryl group, an alkoxy group or a halogen;

L is a substituted or unsubstituted (C_1-C_{40}) hydrocarbylene or a substituted or unsubstituted (C_1-C_{40}) heterohydrocarbylene, wherein the substituted or unsubstituted (C_1-C_{40}) hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone, linking the two Z groups in Structure H2a (to which L 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 two Z groups in Structure H2a, wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone of the substituted or unsubstituted (C_1-C_{40}) heterohydrocarbylene, independently, is a carbon atom or 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, independently, each R^C is 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 H2a is independently a substituted or unsubstituted (C_1-C_{30}) hydrocarbyl, a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl, or $-H$; and

and each of Z^1 and Z^2 is independently selected from $-S$, $-N(R^N)$, or $-P(R^P)$, wherein R^N and R^P are defined above.

F] The process of A]-E] above, wherein, the metal complex H is selected from the following formulas h1a1, h1a2, h1a3, h1b1, h1b2, h1b3, h2a1 or h2a2 (note: Bn = benzyl group ($Ph-CH_2-$)):



- G] The process of any one of A]-F] above, wherein the metal complex S is selected from Formula S1, and further Formula S1a.
- H] The process of any one of A]-F] above, wherein the metal complex S is selected from Formula S2, and further Formula S2a.
- I] The process of any one of A]-F] above, wherein the metal complex S is selected from Formula S3.
- J] The process of any one of A]-F] above, wherein the metal complex S is selected from Formula S4.
- K] The process of any one of A]-F] above, wherein the metal complex S is selected from Formula S5.
- L] The process of any one of A]-K] above, wherein the metal complex H is selected from Formula H1, and further Formula H1a or Formula H1b.
- M] The process of any one of A]-K] above, wherein the metal complex H is selected from Formula H2, and further Formula H2a.
- N] The process of any one of A]-M] above, 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.
- O] The process of any one of A]-N] above, wherein the at least one chain shuttling agent is selected from the following: $\text{Zn}(\text{CH}_2\text{CH}_3)_2$, $\text{Al}(\text{CH}_2\text{CH}_3)_3$, an Al-DHCSA, a ZnAl-DHCSA or a combination thereof, and further an Al-DHCSA, a ZnAl-DHCSA or a combination thereof.
- P] The process of any one of A]-O] above, wherein the at least one chain shuttling agent is added to reactor A.
- Q] The process of any one of A]-O] above, wherein the at least one chain shuttling agent is added to reactor B.
- R] The process of any one of A]-O] above, wherein the at least one chain shuttling agent is added to both reactor A and reactor B.
- S] The process of any one of A]-R] above, wherein step A occurs before step B.
- T] The process of S] above, wherein unreacted monomer in reactor B is recycled back to reactor A.
- U] The process of any one of A]-R] above, wherein step B occurs before step A.
- V] The process of U] above, wherein unreacted monomer in reactor A is recycled back to reactor B.

W] The process of any one of A]-V] above, wherein, the polymerization is a solution polymerization, and further a continuous solution polymerization.

X] The process of any one of A]-W] above, wherein, in reactor A, the polymerization takes place at a temperature $\geq 90^{\circ}\text{C}$, or $\geq 95^{\circ}\text{C}$, or $\geq 100^{\circ}\text{C}$, or $\geq 105^{\circ}\text{C}$, or $\geq 110^{\circ}\text{C}$, or $\geq 115^{\circ}\text{C}$.

Y] The process of any one of A]-X] above, wherein, in reactor A, the polymerization takes place at a temperature $\leq 200^{\circ}\text{C}$, or $\leq 190^{\circ}\text{C}$, or $\leq 180^{\circ}\text{C}$, or $\leq 170^{\circ}\text{C}$, or $\leq 160^{\circ}\text{C}$, or $\leq 150^{\circ}\text{C}$, or $\leq 145^{\circ}\text{C}$, or $\leq 140^{\circ}\text{C}$, or $\leq 135^{\circ}\text{C}$, or $\leq 130^{\circ}\text{C}$, or $\leq 125^{\circ}\text{C}$.

Z] The process of any one of A]-Y] above, wherein, in reactor B, the polymerization takes place at a temperature $\geq 90^{\circ}\text{C}$, or $\geq 95^{\circ}\text{C}$, or $\geq 100^{\circ}\text{C}$, or $\geq 105^{\circ}\text{C}$, or $\geq 110^{\circ}\text{C}$, or $\geq 115^{\circ}\text{C}$.

A2] The process of any one of A]-Z] above, wherein, in reactor B, the polymerization takes place at a temperature $\leq 200^{\circ}\text{C}$, or $\leq 190^{\circ}\text{C}$, or $\leq 180^{\circ}\text{C}$, or $\leq 170^{\circ}\text{C}$, or $\leq 160^{\circ}\text{C}$, or $\leq 150^{\circ}\text{C}$, or $\leq 145^{\circ}\text{C}$, or $\leq 140^{\circ}\text{C}$, or $\leq 135^{\circ}\text{C}$, or $\leq 130^{\circ}\text{C}$, or $\leq 125^{\circ}\text{C}$.

B2] The process of any one of A]-A2] above, wherein the polymerization in reactor A takes place at a pressure ≥ 90 psig, or ≥ 100 psig, or ≥ 110 psig, or ≥ 120 psig, or ≥ 130 psig, or ≥ 140 psig, or ≥ 150 psig, or ≥ 160 psig, or ≥ 170 psig, or ≥ 180 psig.

C2] The process of any one of A]-B2] above, wherein the polymerization in reactor A takes place at a pressure ≤ 250 psig, or ≤ 240 psig, or ≤ 230 psig, or ≤ 220 psig, or ≤ 210 psig, or ≤ 200 psig.

D2] The process of any one of A]-C2] above, wherein the polymerization in reactor B takes place at a pressure ≥ 90 psig, or ≥ 100 psig, or ≥ 110 psig, or ≥ 120 psig, or ≥ 130 psig, or ≥ 140 psig, or ≥ 150 psig, or ≥ 160 psig, or ≥ 170 psig, or ≥ 180 psig.

E2] The process of any one of A]-D2] above, wherein the polymerization in reactor B takes place at a pressure ≤ 250 psi, or ≤ 240 psi, or ≤ 230 psi, or ≤ 220 psi, or ≤ 210 psi, or ≤ 200 psi.

F2] The process of any one of A]-E2] above, wherein, for the ethylene/vinylarene diblock interpolymers or the ethylene/vinylarene triblock interpolymers, the vinylarene is styrene.

G2] The process of any one of A]-F2] above, wherein the mixture A comprises the alpha-olefin.

H2] The process of G2] above, wherein the alpha-olefin is a C3-C20 alpha-olefin, further a C3-C10 alpha-olefin, further a C3-C8 alpha-olefin, further propylene, 1-butene, 1-hexene or 1-octene, further propylene, 1-butene or 1-octene, further 1-butene or 1-octene, further 1-octene.

I2] The process of any one of A]-H2] above, wherein the mixture B comprises the alpha-olefin.

J2] The process of I2] above, wherein the alpha-olefin is a C3-C20 alpha-olefin, further a C3-C10 alpha-olefin, further a C3-C8 alpha-olefin, further propylene, 1-butene, 1-hexene or 1-octene, further propylene, 1-butene or 1-octene, further 1-butene or 1-octene, further 1-octene.

K2] The process of any one of A]-J2] above, wherein the molar ratio of “the metal of complex S” to “the metal of complex H” is ≥ 0.03 , or ≥ 0.1 , or ≥ 0.5 .

L2] The process of any one of A]-K2] above, wherein the molar ratio of “the metal of complex S” to “the metal of complex H” is ≤ 1000 , or ≤ 500 , or ≤ 100 .

M2] The process of any one of A]-L2] above, wherein the molar ratio of “the metal of the chain shuttling agent” to “the sum of the metal of complex S and the metal of complex H” is ≥ 2.0 , or ≥ 5.0 , or ≥ 10 , or ≥ 20 , or ≥ 40 , or ≥ 100 .

N2] The process of any one of A]-M2] above, wherein the molar ratio of “the metal of the chain shuttling agent” to “the sum of the metal of complex S and the metal of complex H” is ≤ 1000 , or ≤ 800 , or ≤ 500 .

O2] The process of any one of A]-N2] above, wherein metal complex S has a reactivity ratio, $r_{(\text{ethylene})(\text{vinylarene})} = k_{(\text{ethylene})(\text{ethylene})}/k_{(\text{ethylene})(\text{vinylarene})}$, from 50 to 1000, further from 100 to 500.

P2] The process of any one of A]-O2] above, wherein metal complex H has a reactivity ratio, $r_{(\text{ethylene})(\text{vinylarene})} = k_{(\text{ethylene})(\text{ethylene})}/k_{(\text{ethylene})(\text{vinylarene})}$, from 1 to 10.

Q2] The process of any one of A]-P2] above, wherein composition further comprises a polyethylene homopolymer, an ethylene/vinylarene copolymer, an ethylene/alpha-olefin copolymer, or a combination thereof.

R2] A composition formed from the process of any one of A]-Q2] above.

A3] A composition comprising an ethylene/vinylarene diblock interpolpolymer or an ethylene/vinylarene triblock interpolpolymer, said diblock interpolpolymer comprising at least one polymer structure selected from Structure 1, as shown below, and said triblock interpolpolymer 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.

B3] The composition of A3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≥ 15 mol%, or ≥ 20 mol%, or ≥ 25 mol%, or ≥ 30 mol%, or ≥ 35 mol%, or ≥ 40 mol%, or ≥ 45 mol%, or ≥ 50 mol%, or ≥ 55 mol%, or ≥ 60 mol%, of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment.

C3] The composition of A3] or B3] above, wherein for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, < 100 mol%, or ≤ 98 mol%, or ≤ 96 mol%, or ≤ 94 mol%, or ≤ 92 mol%, or ≤ 91 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment.

D3] The composition of any one of A3]-C3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≥ 0 mol%, or ≥ 0.2 mol%, or ≥ 0.4 mol%, or ≥ 0.6 mol%, or ≥ 0.8 mol%, or ≥ 1.0 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AP) segment.

E3] The composition of any one of A3]-D3] above, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≤ 10 mol%, or ≤ 9.0 mol%, or ≤ 8.0 mol%, or ≤ 7.0 mol%, or ≤ 6.0 mol%, or ≤ 5.0 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AP) segment.

F3] The composition of any one of A3]-E3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≥ 2.0 mol%, or ≥ 4.0 mol%, or ≥ 6.0 mol%,

or ≥ 8.0 mol%, or ≥ 9.0 mol%, or ≥ 10 mol%, or ≥ 11 mol%, or ≥ 12 mol%, or ≥ 13 mol%, or ≥ 14 mol% of ethylene, based on the total moles of polymerized monomers in the (AR) segment.

G3] The composition of any one of A3]-F3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≤ 80 mol%, or ≤ 77 mol%, or ≤ 75 mol%, or ≤ 73 mol%, or ≤ 70 mol%, or ≤ 65 mol%, or ≤ 60 mol%, or ≤ 55 mol%, or ≤ 50 mol%, or ≤ 45 mol%, or ≤ 40 mol% of ethylene, based on the total moles of polymerized monomers in the (AR) segment.

H3] The composition of any one of A3]-G3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≥ 50 mol%, ≥ 52 mol%, or ≥ 54 mol%, or ≥ 56 mol%, or ≥ 58 mol%, or ≥ 60 mol%, or ≥ 62 mol%, or ≥ 64 mol%, or ≥ 66 mol%, or ≥ 68 mol%, or ≥ 70 mol% of ethylene, based on the total moles of polymerized monomers in the (AP) segment.

I3] The composition of any one of A3]-H3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≤ 100 mol%, or ≤ 98 mol%, or ≤ 96 mol%, or ≤ 94 mol%, or ≤ 92 mol%, or ≤ 90 mol% of ethylene, based on the total moles of polymerized monomers in the (AP) segment.

J3] The composition of any one of A3]-I3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≥ 0 mol%, ≥ 1.0 mol%, or ≥ 2.0 mol%, or ≥ 3.0 mol%, or ≥ 4.0 mol%, of the alpha-olefin, based on the total moles of polymerized monomers in the (AR) segment.

K3] The composition of any one of A3]-J3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment independently comprises, in polymerized form, ≤ 10 mol%, ≤ 9.0 mol%, or ≤ 8.0 mol%, or ≤ 7.0 mol%, or ≤ 6.0 mol%, of the alpha-olefin, based on the total moles of polymerized monomers in the (AR) segment.

L3] The composition of J3] or K3] above, wherein, the alpha-olefin is a C3-C20 alpha-olefin, further a C3-C10 alpha-olefin, further a C3-C8 alpha-olefin, further propylene, 1-butene, 1-hexene or 1-octene, further propylene, 1-butene or 1-octene, further 1-butene or 1-octene, further 1-octene.

M3] The composition of any one of A3]-L3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment does not comprises, in polymerized form, the alpha-olefin.

N3] The composition of any one of A3]-M3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≥ 0 mol%, ≥ 1.0 mol%, or ≥ 2.0 mol%, or ≥ 3.0 mol%, or ≥ 4.0 mol%, or ≥ 6.0 mol%, or ≥ 8.0 mol%, or ≥ 10 mol% of the alpha-olefin, based on the total moles of polymerized monomers in the (AP) segment.

O3] The composition of any one of A3]-N3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment independently comprises, in polymerized form, ≤ 40 mol%, or ≤ 35 mol%, or ≤ 30 mol%, or ≤ 28 mol%, or ≤ 26 mol%, or ≤ 24 mol%, or ≤ 22 mol%, or ≤ 20 mol% of the alpha-olefin, based on the total moles of polymerized monomers in the (AP) segment.

P3] The composition of N3] or O3] above, wherein, the alpha-olefin is a C3-C20 alpha-olefin, further a C3-C10 alpha-olefin, further a C3-C8 alpha-olefin, further propylene, 1-butene, 1-hexene or 1-octene, further propylene, 1-butene or 1-octene, further 1-butene or 1-octene, further 1-octene.

Q3] The composition of any one of A3]-P3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≥ 20 mol%, or ≥ 40 mol%, or ≥ 60 mol%, or ≥ 80 mol%, or ≥ 85 mol%, or ≥ 90 mol%, or ≥ 92 mol%, or ≥ 94 mol%, or ≥ 96 mol%, or ≥ 98 mol%, or ≥ 99 mol% of the polymerized vinylarene in each (AR) segment is present in a "back to back" configuration as shown below in subsegment bb:

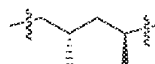


(subsegment bb); and wherein the mol% is based on the total moles of polymerized vinylarene in the (AR) segment.

R3] The composition of any one of A3]-Q3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≤ 100 mol% of the polymerized vinylarene in each (AR) segment is present in a "back to back" configuration as shown below in subsegment bb above.

S3] The composition of any one of A3]-R3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≥ 20 mol%, or ≥ 40 mol%, or ≥ 60 mol%, or ≥ 80 mol%, or ≥ 85 mol%, or ≥ 90 mol%, or ≥ 92 mol%, or ≥ 94 mol%, or ≥ 96 mol%, or ≥ 98 mol%, or ≥ 99 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.

T3] The composition of any one of A3]-S3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≤ 100 mol% of the polymerized vinylarene in each (AR) segment is present in a syndiotactic “back to back” configuration as shown in subsegment sbb above.

U3] The composition of any one of A3]-T3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, ≥ 0 and ≤ 5.0 mol%, or ≤ 2.0 mol%, or ≤ 1.0 mol%, or ≤ 0.5 mol%, or ≤ 0.2 mol%, or ≤ 0.1 mol% 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.

V3] The composition of any one of A3]-U3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, none of the polymerized vinylarene in each (AP) segment is present in a “back to back” configuration as shown in subsegment bb above.

W3] The composition of any one of A3]-V3] above, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, the vinylarene is styrene.

X3] The composition of any one of A3]-W3] above, wherein the ethylene/vinylarene diblock interpolpolymer is an ethylene/alpha-olefin/vinylarene diblock interpolpolymer and further a terpolymer, or the ethylene/vinylarene triblock interpolpolymer is an ethylene/alpha-olefin/vinylarene triblock interpolpolymer and further a terpolymer.

Y3] The composition of any one of A3]-X3] above, wherein the ethylene/vinylarene diblock interpolpolymer, or the ethylene/vinylarene triblock interpolpolymer has a $Tm1 \geq 50^{\circ}\text{C}$, or $\geq 55^{\circ}\text{C}$, or $\geq 60^{\circ}\text{C}$, or $\geq 70^{\circ}\text{C}$, and a $Tm2 \geq 120^{\circ}\text{C}$, or $\geq 124^{\circ}\text{C}$, or $\geq 150^{\circ}\text{C}$, or $\geq 170^{\circ}\text{C}$, or $\geq 200^{\circ}\text{C}$, or $\geq 210^{\circ}\text{C}$, or $\geq 220^{\circ}\text{C}$, or $\geq 230^{\circ}\text{C}$.

Z3] The composition of any one of A3]-Y3] above, wherein the ethylene/vinylarene diblock interpolpolymer, or the ethylene/vinylarene triblock interpolpolymer has a $Tm1 \leq 120^{\circ}\text{C}$, or $\leq 115^{\circ}\text{C}$, or $\leq 110^{\circ}\text{C}$, or $\leq 105^{\circ}\text{C}$, and a $Tm2 \leq 270^{\circ}\text{C}$, or $\leq 265^{\circ}\text{C}$, or $\leq 260^{\circ}\text{C}$, or $\leq 255^{\circ}\text{C}$, or $\leq 250^{\circ}\text{C}$, or $\leq 245^{\circ}\text{C}$.

A4] The composition of any one of A3]-Z3] above, wherein the ethylene/vinylarene diblock interpolpolymer, or the ethylene/vinylarene triblock interpolpolymer has a $Tg1 \geq -70^{\circ}\text{C}$, or $\geq -68^{\circ}\text{C}$, or $\geq -66^{\circ}\text{C}$, or $\geq -64^{\circ}\text{C}$, or $\geq -62^{\circ}\text{C}$, and a $Tg2 \geq 2.0^{\circ}\text{C}$, or $\geq 5.0^{\circ}\text{C}$, or $\geq 10^{\circ}\text{C}$, or $\geq 15^{\circ}\text{C}$, or $\geq 20^{\circ}\text{C}$, or $\geq 30^{\circ}\text{C}$.

B4] The composition of any one of A3]-A4] above, wherein the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer has a $Tg1 \leq -30^{\circ}\text{C}$, or $\leq -32^{\circ}\text{C}$, or $\leq -34^{\circ}\text{C}$, or $\leq -36^{\circ}\text{C}$, or $\leq -38^{\circ}\text{C}$, or $\leq -40^{\circ}\text{C}$, or $\leq -42^{\circ}\text{C}$, or $\leq -44^{\circ}\text{C}$, or $\leq -46^{\circ}\text{C}$, and a $Tg2 \leq 125^{\circ}\text{C}$, or $\leq 120^{\circ}\text{C}$, or $\leq 115^{\circ}\text{C}$, or $\leq 110^{\circ}\text{C}$, or $\leq 105^{\circ}\text{C}$.

C4] The composition of any one of A3]-B4] above, wherein the composition has a molecular weight distribution ($MWD = Mw/Mn$) ≥ 3.0 , or ≥ 3.1 , or ≥ 3.2 , or ≥ 3.3 , or 3.4 , or ≥ 3.6 , or ≥ 3.8 , or ≥ 4.0 .

D4] The composition of any one of A3]-C4] above, wherein the composition has a molecular weight distribution $MWD \leq 50$, or ≤ 45 , or ≤ 40 , or ≤ 38 , or ≤ 36 , or ≤ 34 , or ≤ 32 , or ≤ 30 , or ≤ 28 , or ≤ 26 .

E4] The composition of any one of A3]-D4] above, wherein the composition has a number average molecular weight distribution (Mn) $\geq 4,000$ g/mol, or $\geq 6,000$ g/mol, or $\geq 8,000$ g/mol, or $\geq 10,000$ g/mol, or $\geq 12,000$ g/mol.

F4] The composition of any one of A3]-E4] above, wherein the composition has a $Mn \leq 100,000$ g/mol or $\leq 90,000$ g/mol, or $\leq 80,000$ g/mol, or $\leq 75,000$ g/mol, or $\leq 70,000$ g/mol, or $65,000$ g/mol or $\leq 60,000$ g/mol, or $\leq 55,000$ g/mol, or $\leq 50,000$ g/mol, or $\leq 45,000$ g/mol.

G4] The composition of any one of A3]-F4] above, wherein the composition has a weight average molecular weight distribution (Mw) $\geq 50,000$ g/mol, $\geq 55,000$ g/mol, $\geq 60,000$ g/mol, $\geq 65,000$ g/mol, or $\geq 70,000$ g/mol, or $\geq 75,000$ g/mol, or $\geq 80,000$ g/mol.

H4] The composition of any one of A3]-G4] above, wherein the composition has a $Mw \leq 500,000$ g/mol or $\leq 450,000$ g/mol, or $\leq 400,000$ g/mol, or $\leq 390,000$ g/mol, or $\leq 380,000$ g/mol, or $\leq 370,000$ g/mol, or $\leq 360,000$ g/mol.

I4] The composition of any one of A3]-H4] above, wherein the composition has a melt index ($I2$) ≥ 0.5 dg/min, or ≥ 1.0 dg/min, or ≥ 2.0 dg/min, or ≥ 5.0 dg/min, or ≥ 10 dg/min.

J4] The composition of any one of A3]-I4] above, wherein the composition has a melt index (I2) $\leq 1,000$ dg/min, or ≤ 500 dg/min, or ≤ 250 dg/min, or ≤ 100 dg/min, or ≤ 50 dg/min, or ≤ 20 dg/min.

K4] The composition of any one of A3]-J4] above, wherein the composition has a $T_m \geq 200^\circ\text{C}$, or $\geq 205^\circ\text{C}$, or $\geq 210^\circ\text{C}$, or $\geq 215^\circ\text{C}$, or $\geq 220^\circ\text{C}$, or $\geq 225^\circ\text{C}$, or $\geq 230^\circ\text{C}$, or $\geq 235^\circ\text{C}$.

L4] The composition of any one of A3]-K4] above, wherein the composition has a $T_m \leq 300^\circ\text{C}$, or $\leq 290^\circ\text{C}$, or $\leq 285^\circ\text{C}$, or $\leq 280^\circ\text{C}$, or $\leq 275^\circ\text{C}$, or $\leq 270^\circ\text{C}$, or $\leq 265^\circ\text{C}$.

M4] The composition of any one of A3]-L4] above, wherein the composition has a $T_g \geq -80^\circ\text{C}$, or $\geq -75^\circ\text{C}$, or $\geq -70^\circ\text{C}$, or $\geq -69^\circ\text{C}$, or $\geq -68^\circ\text{C}$, or $\geq -67^\circ\text{C}$.

N4] The composition of any one of A3]-M4] above, wherein the composition has a $T_g \leq -30^\circ\text{C}$, or $\leq -35^\circ\text{C}$, or $\leq -40^\circ\text{C}$, or $\leq -45^\circ\text{C}$, or $\leq -50^\circ\text{C}$, or $\leq -55^\circ\text{C}$, or $\leq -60^\circ\text{C}$.

O4] The composition of any one of A3]-N4] above, wherein the composition comprises, in polymerized form, ≥ 5.0 mol%, or ≥ 10 mol%, or ≥ 12 mol%, or ≥ 14 mol%, or ≥ 16 mol% of the vinylarene, based on the total moles of polymerized monomers in the composition.

P4] The composition of any one of A3]-O4] above, wherein the composition comprises, in polymerized form, < 50 mol%, or ≤ 45 mol%, or ≤ 40 mol%, or ≤ 35 mol%, or ≤ 30 mol% of the vinylarene, based on the total moles of polymerized monomers in the composition.

Q4] The composition of any one of A3]-P4] above, wherein the composition comprises, in polymerized form, ≥ 30 mol%, or ≥ 35 mol%, or ≥ 40 mol%, or ≥ 42 mol%, or ≥ 44 mol%, or ≥ 46 mol%, or ≥ 48 mol%, or ≥ 50 mol% of ethylene, based on the total moles of polymerized monomers in composition.

R4] The composition of any one of A3]-Q4] above, wherein the composition comprises, in polymerized form, < 90 mol%, or ≤ 85 mol%, or ≤ 80 mol%, or ≤ 78 mol%, or ≤ 76 mol%, or ≤ 74 mol%, or ≤ 72 mol%, or ≤ 70 mol%, or ≤ 68 mol% of ethylene, based on the total moles of polymerized monomers in the composition.

S4] The composition of any one of A3]-R4] above, wherein the composition comprises, in polymerized form, ≥ 2.0 mol%, ≥ 5.0 mol%, or ≥ 10 mol%, or ≥ 12 mol%, or ≥ 14 mol%, or ≥ 16 mol%, or ≥ 18 mol%, or ≥ 20 mol% of the alpha-olefin, based on the total moles of polymerized monomers in the composition.

T4] The composition of any one of A3]-S4] above, wherein the composition comprises, in polymerized form, ≤ 50 mol%, or ≤ 45 mol%, or ≤ 40 mol%, or ≤ 35 mol%, or ≤ 30 mol%, or ≤ 28 mol% of the alpha-olefin, based on the total moles of polymerized monomers in the composition.

U4] The composition of S4] or T4] above, wherein, the alpha-olefin is a C3-C20 alpha-olefin, further a C3-C10 alpha-olefin, further a C3-C8 alpha-olefin, further propylene, 1-butene, 1-hexene or 1-octene, further propylene, 1-butene or 1-octene, further 1-butene or 1-octene, further 1-octene.

V4] The composition of any one of A3]-U4] above, wherein for the composition, the molar ratio of block styrene (b-b in AR) to isolated styrene is ≥ 2.0 mol%, ≥ 4.0 mol%, or ≥ 6.0 mol%, or ≥ 8.0 mol%, or ≥ 10 mol.

W4] The composition of any one of A3]-V4] above, wherein, for the composition, the molar ratio of block styrene (b-b in AR) to isolated styrene is ≤ 30 mol%, or ≤ 25 mol%, or ≤ 20 mol%, or ≤ 18 mol%, or ≤ 16 mol%, or ≤ 14 mol%, or ≤ 12 mol%.

X4] The composition of any one of A3]-W4] above, wherein the vinylarene is styrene.

Y4] The composition of any one of A3]-X4] above, wherein the composition comprises an ethylene/vinylarene diblock interpolpolymer, and further an ethylene/vinylarene diblock terpolymer.

Z4] The composition of any one of A3]-Y4] above, wherein the composition comprises an ethylene/vinylarene triblock interpolpolymer, and further an ethylene/vinylarene triblock terpolymer.

A5] The composition of any one of A3]-Z4] above, wherein composition further comprises a polyethylene homopolymer, an ethylene/vinylarene copolymer, an ethylene/alpha-olefin copolymer, or a combination thereof.

B5] The composition of any one of A3]-A5] above, wherein the composition further comprises a thermoplastic polymer, different from the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer in one or more features, such as monomer(s) types and/or amounts, T_m , T_g , M_n , M_w , MWD, or any combination thereof, and further, in one or more features, such as monomer(s) types and/or amounts, T_m , T_g , or any combination thereof.

C5] An article comprising at least one component formed from the composition of any one of R2] or A3]-B5] above.

D5] A process to form the composition of any one of A3]-A5] above, said process comprising the following:

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, each as described above;

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, each as described above;

wherein step A occurs before step B, and at least a portion, and further ≥ 50 wt%, or ≥ 80 wt%, or ≥ 90 wt%, or ≥ 98 wt%, of the reactor product in reactor A is transferred to reactor B; or step B occurs before step A, and at least a portion, and further ≥ 50 wt%, or ≥ 80 wt%, or ≥ 90 wt%, or ≥ 98 wt%, of the reactor product in reactor B is transferred to reactor A; and wherein each wt% is based on the total weight of the respective reactor product; 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.

TEST METHODS

Gel Permeation Chromatography (Conventional)

The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph, equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 160° Celsius, and the column compartment was set at 150° Celsius. The columns were four AGILENT "Mixed A" 30 cm, 20-micron linear mixed-bed columns. The chromatographic solvent was 1,2,4-trichlorobenzene, which contained "200 ppm" of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters, and the flow rate was 1.0 milliliters/minute.

Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards, with molecular weights ranging from 580 to 8,400,000, and which were arranged in six "cocktail" mixtures, with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at "0.025 grams in 50 milliliters" of solvent, for molecular weights equal to, or greater than, 1,000,000, and at "0.05 grams in 50 milliliters" of solvent, for molecular weights less than 1,000,000. The polystyrene standards were dissolved at 80° Celsius, with gentle agitation, for 30 minutes. The polystyrene

standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (\text{EQ1}), \text{ where } M \text{ is the molecular weight,}$$

A has a value of 0.4315 and B is equal to 1.0.

A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points. A small adjustment to A (from approximately 0.375 to 0.445) was made to correct for column resolution and band-broadening effects, such that linear homopolymer polyethylene standard is obtained at 120,000 Mw. The total plate count of the GPC column set was performed with decane (prepared at “0.04 g in 50 milliliters” of TCB, and dissolved for 20 minutes with gentle agitation). The plate count (Equation 2) and symmetry (Equation 3) were measured on a “200 microliter injection,” according to the following equations:

$$\text{Plate Count} = 5.54 * \left(\frac{(RV_{\text{Peak Max}})}{\text{Peak Width at } \frac{1}{2}\text{height}} \right)^2 \quad (\text{EQ2}), \text{ where RV is the retention volume}$$

in milliliters, the peak width is in milliliters, the peak max is the maximum height of the peak, and $\frac{1}{2}$ height is $\frac{1}{2}$ height of the peak maximum; and

$$\text{Symmetry} = \frac{(\text{Rear Peak } RV_{\text{one tenth height}} - RV_{\text{Peak max}})}{(RV_{\text{Peak max}} - \text{Front Peak } RV_{\text{one tenth height}})} \quad (\text{EQ3}), \text{ where RV is the retention}$$

volume in milliliters, and the peak width is in milliliters, Peak max is the maximum position of the peak, one tenth height is 1/10 height of the peak maximum, and where rear peak refers to the peak tail at later retention volumes than the peak max, and where front peak refers to the peak front at earlier retention volumes than the peak max. The plate count for the chromatographic system should be greater than 18,000, and symmetry should be between 0.98 and 1.22.

Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples (weight-targeted at “2 mg/ml”) and the solvent (contained 200 ppm BHT) were added to a pre nitrogen-sparged, septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for two hours at 160° Celsius under “low speed” shaking.

The calculations of $M_{n(\text{GPC})}$, $M_{w(\text{GPC})}$, and $M_{z(\text{GPC})}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 4-6, using the PolymerChar GPCOne™ Software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1. Equations 4-6 are as follows:

$$Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(\frac{IR_i}{M_{polyethylene_i}} \right)} \quad (\text{EQ 4}), \quad Mw_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (\text{EQ 5}), \text{ and}$$

$$Mz_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (\text{EQ 6}).$$

In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample, via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample, by RV alignment of the respective decane peak within the sample (RV(FM Sample)), to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak were then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. To facilitate the highest accuracy of a RV measurement of the flow marker peak, a least-squares fitting routine was used to fit the peak of the flow marker concentration chromatogram to a quadratic equation. The first derivative of the quadratic equation was then used to solve for the true peak position. After calibrating the system, based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) was calculated as Equation 7: Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample)) (EQ7). Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.7% of the nominal flowrate.

Melt Index

The melt index (I2) of an ethylene-based polymer is measured in accordance with ASTM D-1238, condition 190°C/2.16 kg. The melt flow rate (MFR) of a propylene-based polymer is measured in accordance with ASTM D-1238, condition 230°C/2.16 kg.

Density

ASTM D4703 is used to make a polymer plaque for density analysis. ASTM D792, Method B, is used to measure the density of the polymer.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is used to measure Tm, Tc, Tg and crystallinity in ethylene-based (PE) polymer samples and styrene-based (PS) polymer

samples. About 5 to 8 mg of polymer sample was weighed and placed in a DSC pan. The lid was crimped on the pan to ensure a closed atmosphere. Unless otherwise stated, the sample pan was placed in a DSC cell, and then heated, at a rate of 10°C/min, to a temperature of 180°C for PE (300°C for PS). The sample was kept at this temperature for three minutes. Then the sample was cooled at a rate of 10°C/min to -90°C for PE (-90°C for PS), and kept isothermally at that temperature for three minutes. The sample was next heated at a rate of 10°C/min, until complete melting (second heat). Unless otherwise stated, melting point (T_m) and the glass transition temperature (T_g) of each polymer were determined from the second heat curve, and the crystallization temperature (T_c) was determined from the first cooling curve. The T_m (peak temperature) and the T_g were recorded. The percent crystallinity can be calculated by dividing the heat of fusion (H_f), determined from the second heat curve, by a theoretical heat of fusion of 292 J/g for PE (53 J/g for syndiotactic PS), and multiplying this quantity by 100 (for example, % cryst. = (H_f / 292 J/g) x 100 (for PE)).

¹³C NMR

Each sample was prepared by adding approximately 2.7 g of stock solvent to 0.2 g of sample (polymer or polymer composition or metal complex) in a 10 mm NMR tube. The stock solvent was tetrachlorethane-*d*₂ containing 0.025 M chromium acetylacetonate (relaxation agent). The sample was capped and sealed with TEFLON tape. The sample was dissolved and homogenized, by heating the tube and its contents at 130-135°C. The data were collected using a Bruker 600 MHz spectrometer equipped with a Bruker high-temperature CryoProbe. The data were acquired using a 7.3 sec pulse repetition delay (6 sec delay + 1.3 sec acq. time), 90 degree flip angles, and an inverse gated decoupling, with a sample temperature of 120°C. All measurements were made on non-spinning samples in locked mode. Samples were homogenized immediately prior to insertion into a heated (125°C) NMR sample changer, and were allowed to thermally equilibrate in the probe for seven minutes prior to data acquisition.

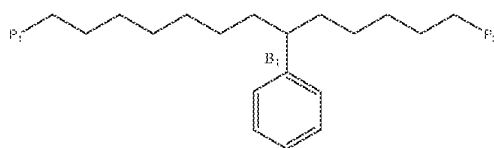
For each sample (polymer or polymer composition) analysis, B1 carbon (quaternary carbon on the aromatic ring) signals from 145.0 to 147.7 ppm were used as styrene contribution, and the molar amounts of polymerized monomers were calculated as follows (S = styrene, E = ethylene):

$$S_{mol} = \text{Integral (145.0 - 147.7 ppm)}$$

$$E_{mol} = (\text{Integral (20.0 - 48.0 ppm)} - 2 * S_{mol})/2$$

$$S \text{ mol\%} = 100 * S_{mol}/(S_{mol}+E_{mol})$$

$$E \text{ mol\%} = 100 - S \text{ mol\%}$$



For each sample (polymer or composition) analysis, B1-4 ring carbon signals from 124.0 to 148.0 ppm were used as styrene contribution, 2B6 (22.0 - 23.5 ppm), and 3B6 (31.5 - 32.7 ppm) signals were used as octene contribution, and the molar amounts of polymerized monomers were calculated as follows (S = styrene, E = ethylene, O = octene):

$$Smol = \text{Integral (124.0 - 148.0 ppm)}/6$$

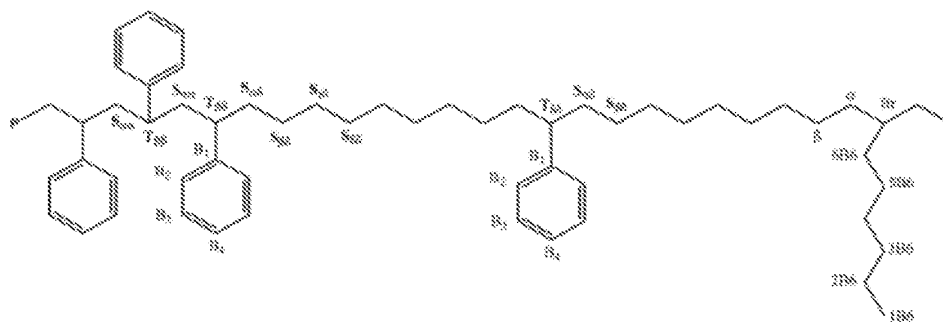
$$Omol = (\text{Integral (22.0 - 23.5 ppm)} + \text{Integral (31.5 - 32.7 ppm)})/2$$

$$Emol = (\text{Integral (11.8 - 48.0 ppm)} - 2*Smol - 8*Omol)/2$$

$$Smol\% = 100*Smol/(Smol+Omol+Emol)$$

$$Omol\% = 100*Omol/(Smol+Omol+Emol)$$

$$Emol\% = 100 - Smol\% - Omol\%$$



$$\text{Average styrene block length} = 2 * (\text{Integrals } T_{pp} + T_{ps}) / \text{Integral } T_{ss}$$

$$\text{The ratio of block styrene to isolated styrene} = (\text{Integrals } T_{pp} + T_{ps}) / \text{Integral } T_{ss}$$

T_{pp} signals are methine signals centered around 41.6 ppm, T_{ps} signals are methine signals centered around 43.9 ppm, and T_{ss} signals are methine signals centered around 46.4 ppm.

$$T_{pp}\% = 100 * \text{Integral } T_{pp} / \text{Integral } B1$$

¹H NMR

Each sample was prepared by adding 130 mg of sample (polymer or polymer composition or metal complex) to 3.25 g of tetrachlorethane-d₂ with 0.001 M Cr(AcAc)₃ in a 10 mm NMR tube. The sample was purged by bubbling N₂ through the solvent, via a pipette inserted into the tube, for approximately 5 minutes, to prevent oxidation. The sample container was capped, and sealed with TEFLON tape. The samples were heated and vortexed at 115°C to ensure homogeneity. ¹H NMR was performed on a Bruker AVANCE 600 MHz

spectrometer equipped with a Bruker high-temperature CryoProbe, and at a sample temperature of 120°C. ^1H NMR was run with ZG pulse, 4 scans, SWH 10,000 Hz, AQ 1.64s, D1 14s.

Compression Molding

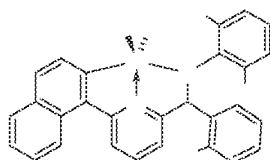
Each polymer composition was compression molded, using a Carver press, into a plaque for physical testing. Each compositions was compression molded according to ASTM D4703 at 190°C with controlled cooling at 15°C/min.

Microtensile Test – Mechanical Properties

Samples were punched from compression molded plaques using the ASTM die D1708. Specimens were tested according to ASTM D1708 at a test speed of 5 in/min.

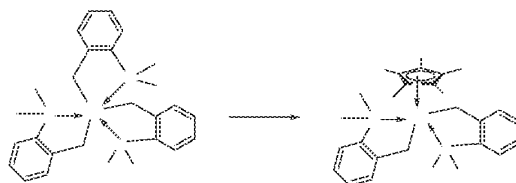
EXPERIMENTAL

I. Catalysts and Chain Shuttling Agents



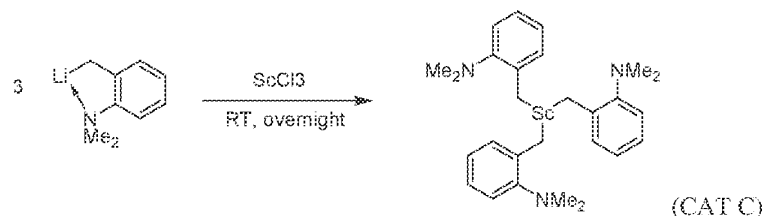
CAT A (See WO03/40195, WO04/24740 and US 8,501,885)

Synthesis of $(\text{C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$, CAT B



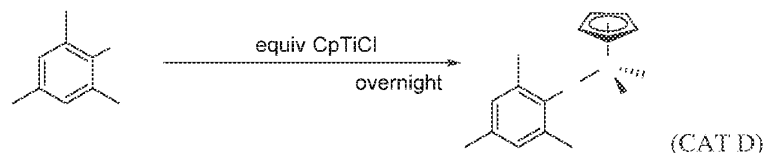
In a nitrogen-filled glovebox, a THF solution (1 mL) of $\text{Sc}(\text{CH}_2\text{CH}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ (0.300 g, 0.67 mmol) was added to a THF solution (1 mL) of $\text{C}_5\text{Me}_5\text{H}$ (0.105 mL, 0.67 mmol) in a 20 mL vial. The solution was heated at 70°C for 12 hours. The solvent was removed under reduced pressure, the residue was extracted with hexane, and then filtered. A concentrated hexane solution was equilibrated at -30°C to give yellow crystals (0.203 g, 65.5% yield). The ^1H NMR and the ^{13}C NMR spectra are consistent with literature reports (Chem. Commun. 2007, 40, 4137-4139). See Figure 2 (^1H NMR) and Figure 3 (^{13}C NMR) of the Sc complex (CAT B).

Synthesis of $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_3$, CAT C, Catalyst for Atactic Polystyrene and Chain Shuttling with Zinc



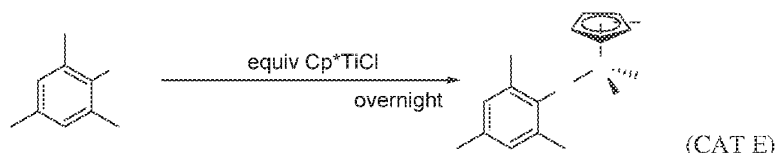
Synthesis of $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_3$: Anhydrous ScCl_3 (1.938 g, 12.81 mmol) was suspended in 10 mL THF. A THF solution (20 mL) of $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o}$ (5.423 g, 28.43 mmol, 3 equiv.) was slowly added at room temperature. After stirring this mixture for 30 minutes, the solvent was removed under reduced pressure. The residue was dissolved in 40 mL of toluene, and then filtered to remove lithium salts. Solvent was removed from the filtrate under reduced pressure, and the residue was washed thoroughly with ether, filtered, and dried, to yield the product as a fine yellow solid. Yield = 2.17 g (38%). ^1H NMR (400 MHz, Benzene- d_6) δ 7.05 – 6.94 (m, 6H), 6.85 – 6.76 (m, 6H), 2.28 (s, 18H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, Benzene- d_6) δ 143.43, 143.15, 129.41, 126.67, 119.95, 117.89, 52.30 – 46.32 (m), 45.04.

Synthesis of Ti Complexes:

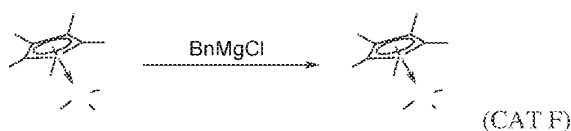


CAT D: The following procedure was performed in a glove box under a nitrogen atmosphere. In an oven-dried, 40 mL vial, equipped with a stir bar, Cp^*TiCl_3 (300 mg, 1.37 mmol) was dissolved in 5.2 mL of anhydrous diethyl ether. This solution was cooled in the glove box freezer for 30 minutes. Lithium 2,4,6-trimethoxy-phenoxy (184 mg, 1.37 mmol) was added to the CpTiCl_3 solution with vigorous stirring. The reaction was allowed to warm to room temperature, and the reaction was stirred overnight at room temperature. The reaction was then filtered, and the solids were washed with 2 mL of anhydrous diethyl ether. The filtrate and washes were combined. The volatiles were removed under vacuum, and a red solid was isolated. This material was analyzed by ^1H NMR spectroscopy; the crude material appeared to contain unreacted CpTiCl_3 . The crude product was dissolved in a minimal amount of methylene chloride, and this solution was then layered with ether. This

solution was placed in the freezer overnight. The desired complex was isolated as red crystals (250 mg, 57%). The produce was analyzed by ^1H NMR spectroscopy [(400 MHz, C_6D_6) δ 6.57 (s, 2H), 6.01 (s, 5H), 2.16 (s, 6H), 2.08 (s, 3H)].



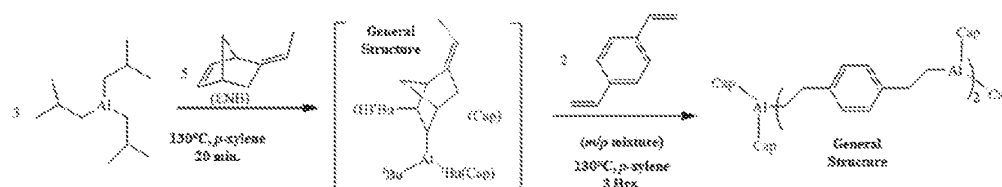
CAT E: The following procedure was performed in a glove box under a nitrogen atmosphere. In an oven-dried, 40 mL vial, equipped with a stir bar, Cp^*TiCl_3 (400 mg, 1.38 mmol) was dissolved in 19 mL of anhydrous diethyl ether. This solution was cooled in the glove box freezer for 30 minutes. Lithium 2,4,6-trimethoxy-phenoxy (196 mg, 1.38 mmol) was added to the Cp^*TiCl_3 solution with vigorous stirring. The reaction was allowed to warm to room temperature, and the reaction was stirred overnight at room temperature. The reaction was then filtered, and the solids were washed with 5 mL of anhydrous diethyl ether. The filtrate and washes were combined. The volatiles were removed under vacuum, and a red solid was isolated. This material was analyzed by ^1H NMR spectroscopy. The crude product was dissolved in a minimal amount of methylene chloride, and this solution was then layered with ether. This solution was placed in the freezer overnight. The desired complex was isolated as red crystals (301 mg, 56%). The produce was analyzed by ^1H NMR spectroscopy [(400 MHz, C_6D_6) δ 6.61 (s, 2H), 2.29 (s, 6H), 2.10 (s, 3H), 1.90 (s, 15H)]. Note: This material contained some unreacted Cp^*TiCl_3 that appeared to co-crystallize with the desired compound.



CAT F: In an oven-dried vial, equipped with a stir bar, Cp^*TiCl_3 (200 mg, 0.69 mmol) was dissolved in 7.5 mL of anhydrous ether. The solution was placed in the glove box freezer for 20 minutes. The vial was then removed from the freezer. To the cooled, stirred solution, a 2.0 M solution of benzylmagnesium chloride (1.0 mL, 2.1 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature, and was stirred for one hour at room temperature. The reaction mixture was filtered to remove the solids, and the yellow solution was reduced under vacuum. A reddish, brown solid was isolated and

analyzed by ^1H NMR spectroscopy [^1H NMR (400 MHz, Benzene- d_6) δ 6.93 (t, $J = 7.3$ Hz, 3H), 6.83 – 6.78 (m, 5H), 2.74 (d, $J = 2.7$ Hz, 6H), 1.62 (d, $J = 0.7$ Hz, 13H).] Note: aromatic protons overlapped with benzene solvent peak.

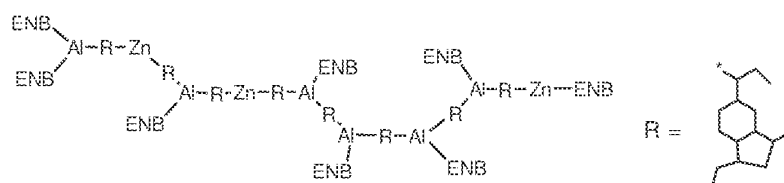
Synthesis of Al-DHCSA



In a glass vial, $\text{Al}(\text{iBu})_3$ (3.00 g, 15.13 mmol) and ENB (3.030 g, 25.21 mmol) were mixed with p -xylene (7 mL). This mixture was heated to 130°C for 20 minutes. Venting of the i -butene was permitted. The mixture of p,m -divinylbenzene (Alfa Aesar 80:20) (1.313 g, 10.08 mmol) was then added, and the mixture allowed to equilibrate at 130°C for an additional three hours, and then cooled to room temperature. Following the reaction period (3 hrs), the temperature of the mixture was cooled to room temperature, and the resulting homogeneous solution used as a DHCSA.

Other chain shuttling agents (CSAs) used in experiments herein, include diethyl zinc (DEZ) and triethyl aluminum (TEA).

ZnAl-DHCSA (see WO2018/064546)



(* point of attachment to a metal; mixture of isomers)

II. Screening Catalyst

PPR Screening of Sc Complex (CAT B) for Hard Blocks

A Parallel Pressure Reactor (PPR) system was employed, in order to demonstrate the viability of styrene polymerization activity and chain shuttling ability of the polymerization catalyst. The activity and molecular weight of a given styrene polymerization catalyst relative to the chain shuttling agent (CSA) loading was investigated. The chain shuttling agents studied were diethylzinc (DEZ) and triethylaluminum (TEA), as models for polymeryl

alkylzinc or polymeryl alkylaluminum species, respectively. Al-Zn DHCSA was also used. PPR screening conditions were as follows: [ISOPAR-E+ MMAO-3A + T] + (Styrene + CSA + “amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluoro-phenyl)borate(1-) + Catalyst); Catalyst Loading = 0.25 μ moles; MMAO-3A Loading = 5 μ moles; T = 105°C, t = 15 minutes, [Styrene] = 2.1 M (in toluene).

CAT B was screened in the PPR for its ability to polymerize styrene in the presence of various model chain shuttling agents. Figure 4 demonstrates that CAT B exhibits high efficiency for styrene polymerization (no CSA), and the catalyst activity is not affected by the addition of the TEA (3rd circle from top at CSA = 25 μ moles, and 3rd and 4th circles from top at CSA = 100 μ moles) or the Al-Zn DHCSA (upper two merged circles at CSA = 25 μ moles, and upper two circles at CSA = 100 μ moles). For this particular study, the catalyst activity was low in the presence of DEZ (two merged lower circles at CSA = 25 μ moles and two merged lower circles at CSA = 100 μ moles). The data in Figure 5 shows that the addition of CSA results in a decrease in the molecular weight, indicating the catalyst participates in effective chain shuttling. Note, the Al-Zn DHCSA is represented by two upper circles at CSA = 25 μ moles, and two upper circles at CSA = 100 μ moles. The TEA is represented by two merged lower circles at CSA = 25 μ moles and two merged lower circles at CSA = 100 μ moles.

Table 1 further depicts the effect of the addition of 100 μ moles of CSA on a styrene polymerization with CAT B at 105°C. In addition, the polymerization of styrene by CAT B was examined in the presence of 1-octene. PPR screening conditions were as follows: T = 105°C, Catalyst Loading = 0.25 μ moles, [Styrene] = 2.1 M (in toluene), t = 15 minutes. As shown in Table 1, the catalyst activity and molecular weight were unaffected by the addition of 1-octene, which indicates that CAT B is compatible with residual alpha-olefin monomer, transferred from the first reactor to the second reactor. This data demonstrates that catalyst CAT B meets the desired second reactor (R2) catalyst criteria (a-c)) described above (see Detailed Description of the Invention).

Table 1: Effect of CSA and 1-Octene on the Polymerization of Styrene with CAT B.

CSA (100 μ moles) or 1-Octene	((g Polymer (PS) per g M)/hr)	Mw (g/mol)
none	149,000	1,300,000
Et ₃ Al (CSA)	100,000	7,900
1-Octene	151,000	1,195,000

M= metal of catalyst (Sc)

Chain Shuttling Experiments for Sc Catalyst: CAT B

A glass vial was charged with toluene (final volume 8 mL), styrene (1 mL), and a

magnetic stir bar. CAT B (5 μ mol), “amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) (1.2 equiv (equiv. to CAT B)), and either TEA or DEZ (0, 25 μ mol, or 100 μ mol) were sequentially added to the solution. This mixture was heated at 100°C for one hour, then allowed to cool, before being quenched in methanol. Polymer was collected by filtration and dried under vacuum. GPC results are shown in Figure 6. Results are also shown in Table 2. A chain shuttling process takes place, as indicated by the decrease in molecular weight and decrease in MWD (Mw/Mn) in the presence of DEZ or TEA, as compared to sPS-1.

Table 2: Syndiotactic Polystyrene (sPS) Prepared with and without Zinc and Aluminum Chain Shuttling Agents

	CSA, umol	Mn (g/mol)	Mw (g/mol)	Mw/Mn	Tg (°C)	Tm (°C)	ΔH_m (°C)	Activity ((g sPS/mol Sc)/hr)	Yield sPS (%)
sPS-1	None	123,761	411,704	3.33	99	271	20.8	152,222	90
sPS-2	DEZ, 25	13,331	27,143	2.04	95	271	29.8	191,296	100
sPS-3	DEZ, 100	5,029	7,903	1.57	97	257	24.5	166,296	99
sPS-4	TEA, 25	22,299	64,039	2.87	96	272	28.1	157,407	94
sPS-5	TEA, 100	7,433	16,790	2.26	95	266	29.2	147,407	88

III. Vinylarene-Rich (Hard Block) Analysis and Vinylarene-Poor (Soft Block) Analysis

Batch Reactor Polymerization Set-Up

The batch reactor set-up consisted of a 600 mL Parr reactor controlled by a process control system. The reactor was equipped with an electric heating jacket, an internal cooling coil for temperature control, and electric heat traced transfer lines between the reactor and the reactor dump pot. Three feeds were available, with the option to load solvents or monomers from a detachable one liter cylinder (50 mL). This cylinder was loaded in an inert (N₂) glove box, and its contents transferred to the reactor via a nitrogen injection. Catalyst components and chain shuttling agents were prepared in the inert glove box, and transferred from the 50 mL cylinder, via a nitrogen transfer, to the reactor. The “1-octene cylinders” were filled from purified plant feeds. Ethylene was supplied from Airgas, as high purity grade. For further purification, the 1-octene and ethylene were passed through inline beds of activated alumina, 13X molecular sieves, and Q5 material. The high pressure nitrogen, for the catalyst injection and purging, was ultra-high purity grade. Styrene was degassed, and the inhibitor was removed by passing the styrene supply through a plug of neutral alumina, just prior to addition into the reactor.

Ethylene, 1-Octene, Styrene Polymerization: Reactivity of CAT B (Vinylarene-Rich)

Degassed, anhydrous toluene was added to the 600 mL Parr reactor from a solvent cylinder, pressurized with nitrogen, using a mass flow meter, and the reactor agitator was set

to 450 rpm. Styrene was injected via a cylinder pressurized with high pressure nitrogen. When used, a preset amount of 1-octene was added to the reactor from a cylinder pressurized with nitrogen, using a flow meter. Once the reactor reached the starting temperature set point of 120°C, a preset amount of ethylene was added to the reactor, using a flow meter, followed by the addition of the active catalyst solution. The catalyst solution was prepared by adding a pre-made toluene solution of Cp*ScR₂ (CAT B) (typical loadings 22 µmol Sc), 0.006 M solution of “amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)-borate(1-)” activator in toluene (1.0-1.2 equiv), and a 0.05 M solution of MMAO-3A in toluene (10 equiv.). Each “equiv” is relative to one equiv. of CAT B.

The flow of ethylene, at 200 mg/min, was initiated, while the overall reactor pressure was controlled at the programmed set point, throughout the desired run time of ten minutes. Following the mixing time, the agitator was stopped, and the contents of reactor were emptied into the dump pot. The pot contents were poured into methanol, and the mixture stirred. The polymer precipitate was filtered and dried at 130°C, in a vacuum oven for six hours. Polymerization conditions and polymer properties are shown in Table 3 below. See also Table 4. The interpolymers AR1-AR12, in Tables 3 and 4, are each representative of an vinylarene-rich (hard block) (AR) segment of an ethylene/octene/-styrene diblock or triblock interpolpolymer, in, for example, monomer composition, tacticity of the polymerized vinylarene, T_m and T_g.

Table 3: [CAT B] Batch Reactor Conditions and GPC, DSC data

Sample	Reactor					GPC					DSC	
	Initial C2, g	Sty, g	C8, g	Tol, g	Yield, g	Efficiency (g poly/g metal)	Mw, g/mol	Mn, g/mol	PDI or MWD	Tg, °C	ΔHm (J/g)	Tm, °C
AR1	10.4	52	22	230	6.2	19987	174,258	21,626	8.06	30	1.85	124
AR2	10.5	94	34	177	0.4	1290	81,351	7,971	10.21	none		
AR3	7	125	67	112	1	2418	91,609	5,322	17.21	96	1.16	233
AR4	6	125	39	148	5.4	11662	119,811	11,461	10.45	103	4.91	241
AR5	5.1	123	17	179	18	29014	390,569	15,255	25.60	92	9.5	241
AR6	10.3	77	50	173	0.282	682	76,315	4,080	18.71	93	0.55	233
AR7	10.4	62	11	234	3	7253	111,994	9,702	11.54	33	0.58	129
AR8	10.4	109	17	184	1.4	3023	79,125	10,209	7.75	102	0.56	218
AR9	5.9	88	76	138	0.335	723	73,127	7,757	9.43	92		
AR10	12.6	47	10	246	0.472	1522	73,583	9,894	7.44	3	2.25	128
AR11	11.6	69	75	148	0.342	739	51,343	9,313	5.51	96		
AR12	10.3	31	17	257	2.5	6045	111,584	23,225	4.80	6	2.47	126

General: Catalyst = 22 μmol [CAT B], 1.2 x 10⁻⁴ amines, bis(hydrogenated tallow alkyl)methyl, tetraakis(pentafluorophenyl)borate(1-), 10x MMAO, T = 120 °C, t = 10 min, V = 600 mL.

Table 4: Polymer Characterization (Cp*Sc Polymers, Syndiotactic PS (100 mol %))

Sample	Styrene, mol % ^a	Octene, mol % ^a	Ethylene, mol % ^a
AR1	41.9	0	58.1
AR2	78.8	0	21.2
AR3	89.8	0	10.2
AR4	90.7	0	9.3
AR5	88.7	0	11.3
AR6	82.3	0	17.7
AR7	50.6	0	49.4
AR8	77.4	0	22.6
AR9	85.7	0	14.3
AR10	33.3	0	66.7
AR11	60	0	40
AR12	27.7	0	72.3

^a Determined by ¹³C NMR, each mol % based on the total moles of polymerized monomers in the interpolymer (represents a vinylarene-rich (Hard Block)).

Ethylene, 1-Octene, Styrene Polymerization: Reactivity of CAT A (Vinylarene-Poor)

Degassed, anhydrous toluene was added to the 600 mL Parr reactor from a solvent cylinder pressurized with nitrogen using a mass flow meter, and the reactor agitator was set to 450 rpm. Styrene was injected via a cylinder pressurized with high pressure nitrogen. A preset amount of 1-octene was added to the reactor from a cylinder pressurized with nitrogen, using a flow meter. Once the reactor reached the starting temperature set point of 120°C, a preset amount of ethylene was added to the reactor using a flow meter, followed by the addition of the active catalyst solution. The catalyst solution was prepared by adding a pre-made toluene solution of CAT A catalyst, 0.006 M solution of “amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)-borate(1-)” activator in toluene (1.0-1.2 equiv), and a 0.05 M solution of MMAO-3A in toluene (10 equiv.). Each “equiv” is relative to one equiv. of CAT A.

The flow of ethylene, at 200 mg/min, was initiated, while the overall reactor pressure was controlled at the programmed setpoint throughout the desired run time of ten minutes. Following the mixing time, the agitator was stopped, and the contents of reactor were emptied into the dump pot. The pot contents were poured into methanol, and the mixture stirred. The polymer precipitate was filtered and dried at 130°C in a vacuum oven for six hours. Polymerization conditions and polymer properties are shown in Table 5 below. See also Table 6. The interpolymers AP1-AP11, in Table 6, are each representative of an vinylarene-poor (Soft Block) (AP) segment of an ethylene/octene/styrene diblock or triblock interpolpolymer, in, for example, monomer composition, tacticity of the polymerized vinylarene, T_m and T_g.

83738-WO-PCT

Table 5: CAT A Batch Reactor Conditions and GPC/DSC Characterization

Sample	Reactor					GPC			DSC		
	Initial C2, g	Sty, g	C8, g	Tol, g	Yield, g	Efficiency (g poly/g metal)	Mw	Mn	PDI or MWD	Tg	DHm (J/g)
AP1	10.4	52	22	230	12	5378	635,434	101,824	6.24	-53	14.44
AP2	10.5	94	34	177	1	448	174,013	60,691	2.87	-48, 105	none
AP3	7	125	67	112	4	1793	229,859	79,968	2.87	-56	none
AP4	5.1	123	17	179	4.3	1927	563,851	179,471	3.14	none	none
AP5	10.3	77	50	173	6.8	3048	1,117,020	221,692	5.04	none	none
AP6	10.4	62	11	234	1	448	235,551	71,309	3.30	96.3	none
AP7	10.4	109	17	184	12.6	5647	401,300	28,850	13.91	-47	5.79
AP8	5.9	88	76	138	13	5827	508,680	124,594	4.08	-61	none
AP9	12.6	47	10	246	12	5378	362,481	96,701	3.75	-49	17.9
AP10	11.6	69	75	148	19	8516	698,512	144,256	4.84	-62	none
AP11	10.3	31	17	257	13	5827	369,706	84,713	4.36	-57	11.26

General: Catalyst = 6-8 μmol CAT A, 1.2 x 10⁻³ amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-)⁻, 10x MMAO, T = 120 °C, t = 10 min, V = 600 mL

Table 6: Polymer Characterization (13C NMR)

Sample	Styrene, mol% ^a	Octene, mol% ^a	Ethylene, mol% ^a
AP1	3.0	11.8	85.3
AP2	1.2	10.5	88.2
AP3	2.7	18.8	78.5
AP4	4.7	7.8	87.5
AP5	2.7	14.3	83.1
AP6	4.3	4.6	91.1
AP7	5.3	8.8	85.9
AP8	5.4	31.7	62.9
AP9	3.1	6.9	90
AP10	3.7	26.9	69.4
AP11	2.2	13.3	84.5

Note: Values of mol% styrene in the table were calculated to include only styrene present in a E/O/S terpolymer with the assumption that no back-to-back styrene was present. This is based on the observation that CAT A does not polymerize styrene under homopolymerization conditions. Any atactic polystyrene was assumed to arise from thermally-generated PS. ^aEach mol% based on the total moles of polymerized monomers in the interpolymer represents a vinylarene-poor (Soft Block).

IV. Dual Catalysts Polymerizations with Chain Shuttling Agent

Batch Reactors Polymerization Set Up (Dual Parr Reactor) – Solution Polymerization

- The polymerization set-up consisted of two reactors, a 600 mL Parr reactor (Reactor 1, R1) and a 2.0 L Parr reactor (Reactor 2, R2), each controlled by a process control system.
- 5 Both reactors were equipped with an electric heating jacket, an internal cooling coil for temperature control, and electric heat traced transfer lines between the reactors and from each reactor to the reactor dump pot. Three feeds were available for either reactor, with the option to load solvents or monomers from a detachable “1 L sample cylinder.” The “1 L cylinder” was loaded in an inert (N₂) glove box, and the contents transferred to either reactor via a
- 10 nitrogen injection. Catalyst components and chain shuttling agents were prepared in the inert glove box, and transferred from a “50 mL cylinder,” via nitrogen transfer, to the respective reactor. ISOPAR-E and 1-octene cylinders were filled from purified plant feeds. Ethylene was supplied from Airgas, as high purity grade. For further purification, the 1-octene and ethylene were passed through inline beds of activated alumina, 13X mole sieves, and Q5
- 15 material. The high pressure nitrogen, for catalyst injection and purging, was ultra-high purity grade.

Batch Reactors – Solution Polymerization – Composition comprising Triblock 2

- The 600 mL Parr reactor (R1 (first reactor)) was charged with a solution of the Al-DHCSA (1.5 mL, 578 μ mol) in 4 mL of ISOPAR-E via high pressure nitrogen injection.
- 20 ISOPAR-E (121.4 g) was added to R1 from a solvent cylinder pressurized with nitrogen, using a mass flow meter, and the reactor agitator was set to 450 rpm. A preset amount of 1-octene (20.4 g) was added to R1 from a cylinder pressurized with nitrogen, using a flow meter. Once the reactor reached the starting temperature set point of 120°C, a preset amount of ethylene (7.1 g) was added to the reactor using a flow meter, followed by the addition of
- 25 the active catalyst solution. The catalyst solution was prepared by adding 0.25 mL of a 0.005 M solution of CAT A in toluene, 0.25 mL of a 0.006 M solution of “amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluoro-phenyl)borate(1-) in toluene, 0.25 mL of a 0.05 M solution of MMAO-3A in toluene, to a vial containing 4 mL of toluene.

- The flow of ethylene, at 200 mg/min, was initiated, while controlling the overall
- 30 reactor pressure at 192.7 psig throughout the desired run time of 10 minutes (for R1). During the R1 run time, the “2.0 L Parr” reactor (R2, second reactor) was charged with 200 mL of toluene, via a small cylinder pressurized with nitrogen. The R2 agitator was set to 450 rpm, and the R2 starting temperature set point to 120°C. When the run time (10 min) in R1 was completed, the agitator was stopped in both reactors (R1 and R2). R1 was pressured with

nitrogen, in order to transfer the contents of R1 to R2 via preheated lines. CAT A (lifetime less than 10 min) was spent, when this catalyst entered the second reactor.

Once the contents were transferred, the R2 agitator was resumed. Styrene monomer (5 mL, 0.044 mol) was injected into R2, via a small cylinder pressurized with nitrogen, immediately followed by the addition of the active catalyst solution in 200 mL of toluene. The catalyst solution was prepared by adding 45 μ mol Sc complex CAT B in toluene, 0.083 mL of a 0.006 M solution of "amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) (0.5 μ mol) in toluene, 0.100 mL of a 0.05 M solution of MMAO-3A (5 μ mol) in toluene, to a vial containing 4 mL of toluene. After the addition of the catalyst, an exotherm was observed. The R2 contents were agitated for a run time of one hour (for R2) at 120°C. Following the reaction time, the R2 agitator was stopped, and the contents of R2 were emptied into the dump pot. The pot contents were poured into methanol and stirred overnight. The polymer precipitate (composition comprising an ethylene/octene/styrene triblock terpolymer (Triblock 2)) was filtered and dried at 130°C in a vacuum oven for six hours (Yield 11.6 g). NMR profiles are shown in Figure 7 (1H NMR) and Figure 8 (13C NMR). Based on peak integration in Figure 7, the composition contained 30 wt% polymerized styrene, based on the weight of the composition. Peaks denoting the phenyl C-1 (δ 145.50), Saa (δ 43.35), and T $\beta\beta$ (δ 40.61) of the syndiotactic polystyrene block are shown in Figure 8.

Additional Polymer Compositions

Additional polymer compositions are described below. Polymerization conditions and polymer composition properties are listed in Tables 7 and 8.

Triblock 1 (composition containing an ethylene/octene/styrene triblock 1 terpolymer) was polymerized using the process above for Triblock 2, except for the following changes. The 600 mL Parr reactor (R1) was charged with a solution of the Al-DHCSA (1.5 mL, 690 μ mol) in 4 mL of ISOPAR-E, via high pressure nitrogen injection. The flow of ethylene, at 200 mg/min, was initiated, while controlling the overall reactor pressure at 192.7 psig throughout the desired run time of 30 minutes (for R1). Styrene monomer (5 mL, 0.690 mmol) was injected into R2 via a small cylinder pressurized with nitrogen, immediately followed by the addition of the active catalyst solution in 200 mL of toluene. The catalyst solution was prepared by adding 0.240 mL of a 0.0021 M solution of Sc complex CAT B (0.5 μ mol) in toluene, 0.083 mL of a 0.006 M solution of "amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)-borate(1-) (0.5 μ mol) in toluene, 0.100 mL of a 0.05 M solution of MMAO-3A (5 μ mol) in toluene, to a vial containing 4 mL of toluene.

The polymer precipitate (composition containing the triblock) was filtered and dried at 130°C in a vacuum oven for six hours (Yield 13.0 g). In order to detect AR-AP coupling (vinylarene-rich (hard block)-vinylarene-poor (soft block)S, a Malvern 305a HT GPC with triple detector (dRI, DV, LS) connected with DiscovIR™ (FT IR) and PDA (UV-Vis) was employed. GPC data is shown in Figure 9 [HT GPC dRI/UV Dual Detector responses for dual batch reactor run showing uncoupled PS, uncoupled EO, and coupled PS.] As seen in Figure 9, the formation of the block interpolmer appears as the “coupled PS” peak.

Triblock 3 (composition containing an ethylene/octene/styrene triblock terpolymer) was prepared according to the process for Triblock 2 as shown above, except for the changes noted in Table 7 below. Diblock 1 (composition containing an ethylene/octene/styrene diblock terpolymer) was prepared according to the process for Triblock 2 as shown above, except TEA (400 μmol) was used as the CSA, and except for the changes noted in Table 7 below. Diblock 2 (composition containing an ethylene/octene/styrene diblock terpolymer) was prepared according to the process for Triblock 2 as shown above, except DEZ (100 μmol) was used as the CSA, and except for the changes noted in Table 7 below.

Two in-reactor blends (IB-1 and IB-2), no CSA, each of an ethylene/octene random copolymer and a syndiotactic styrene-based polymer, were each prepared using the same process as used for Triblock 2 above, but without the Al-DHCSA pre-injection, and except for the changes noted in Table 7 below.

Table 7: Polymerization Conditions and Composition Properties

	CSA	Batch Reactor Run Conditions			GPC Data			DSC Data	
		C2 loading, g	Octene loading, g	Styrene loading, g	Mw (g/mol)	Mn (g/mol)	PDI (MWD)	Tg, °C	Tm, °C
Triblock 2	Al DHCSA	7.1	21.3	5 mL	353,624	13,727	25.76	-	none
Triblock 3	Al DHCSA	8.1	40	40	81,620	23,687	3.45	-67	264
Diblock 1	400 μmol TEA	8.1	40	40	99,948	26,617	3.75	-65	252
Diblock 2	100 μmol DEZ	8.1	40	40	169,726	41,438	4.10	-66	239
IB-2	none	8.1	40	40	96,304	8,759	11.00	72	212

Table 8: 13C NMR Data on Polymer Compositions

	Triblock 2	Triblock 3	Diblock 1	Diblock 2	IB-2
Styrene (mol%) ^a	15.2	14.4	27.7	26.7	19.3
Octene (mol%) ^a	13.2	28.1	27.9	21.8	12.4
Ethylene (mol%) ^a	71.7	57.4	44.4	51.5	68.3
Styrene (wt%) ^b	31.2	24.0	39.7	41.7	37.8
Octene (wt%) ^b	29.1	50.3	43.1	36.7	26.1
Ethylene (wt%) ^b	39.7	25.7	17.1	21.6	36.1
Molar Ratio of block styrene (b-b in AR) to isolated styrene ^c	11.8	53.2*	170.0*	93.1*	32.2

a) Each mol% polymerized monomer based on the total moles of all polymerized monomers in the composition.

b) Each wt% polymerized monomer based on the total weight of all polymerized monomers in the composition.

c) The ratio of block styrene to isolated styrene = (Integrals T₉₅ + T₉₆) / Integral T₆₆. *Almost no T₆₆ detected.

GPC Study

See the above GPC procedure in the Test Methods section. A Polymer Char (Valencia, Spain) high temperature Gel Permeation Chromatography system consisting of an Infrared concentration/composition detector (IR-5) was used for MW and MWD determination. The carrier solvent was 1,2,4-trichlorobenzene (TCB). The auto-sampler and detector compartments were operated at 160°C, and the column compartment was operated at 150°C. Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards. GPC profiles are shown in Figures 10a and 10b. GPC results are shown in Tables 7 and 9. For the molecular weight distributions of dual reactor polymers, values are polystyrene equivalent molecular weights. As seen from Table 9, the composition containing the triblock polymer has a broader MWD as compared to the in-reactor blend (IB-1).

Table 9: GPC (conv.) Results

Composition	Mn (g/mol)	Mp (g/mol)	Mw (g/mol)	Mz (g/mol)	Mw/Mn
Triblock 2	13,727	386,248	353,624	1,092,614	25.76
IB-1	207,112	1,255,515	1,446,647	3,451,127	6.98

Tensile Testing Study

Mechanical properties of two polymer samples are shown in Table 10. See also Figure 11. The samples show elastic recovery behavior.

Table 10: Tensile Testing Data.

Composition	Permanent Set, % Strain	1 st Cycle Hysteresis	2 nd Cycle Hysteresis
Triblock 1	79	73%	53%
Triblock 2	58	70%	56%

V. Atactic Polystyrene (aPS): CAT C

Polymerization Experiments: A glass vial was charged with toluene (final volume 8 mL), styrene (1 mL), and a magnetic stir bar. CAT C (5 μ mol), "amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) (1.2 equiv.), and either TEA or DEZ (0, 25, or 100 μ mol) were sequentially added to the solution. This mixture was heated at 100°C for one hour, then allowed to cool, before being quenched in methanol. Polymer was collected by filtration and dried under vacuum. Results are shown in Table 11. GPC profiles are shown in Figure 12. These results indicate that a chain shuttling process takes place, as indicated by the decrease in molecular weight and decrease in MWD (Mw/Mn) in the presence of DEZ or TEA.

Table 11: Atactic polystyrene (aPS) Prepared with and without a Scandium Catalyst, and in the Presence of Either Zinc or Aluminum Chain Shuttling Agents

	CAT	CSA, μmol	Mn (g/mol)	Mw (g/mol)	Mw/Mn	Tg ($^{\circ}\text{C}$)	Tm ($^{\circ}\text{C}$)	ΔHm ($^{\circ}\text{C}$)	Activity (g PS/mol Sc)	Yield PS (%)
aPS-1	CAT C	None	38,851	100,584	2.59	100	-	-	32,989	31.6
aPS-2	None	None	121,846	223,366	1.83	108	-	-	-	28.2
aPS-3	CAT C	DEZ, 25	4,681	6,622	1.41	82	-	-	23,519	14.0
aPS-4	CAT C	DEZ, 100	4,035	5,759	1.43	78	-	-	63,148	37.5
aPS-5	CAT C	TEA, 25	12,568	181,973	14.48	89	263	2.4	25,185	15.0
aPS-6	CAT C	TEA, 100	-	-	-	89	262	7.9	2,222	1.3

VI. Ti Complexes

5 PPR Screening of Ti complexes (CAT D, CAT E, and CAT F)

The Parallel Pressure Reactor (PPR) system was employed in order to demonstrate the viability of styrene polymerization activity and chain shuttling of each polymerization catalyst as noted below. The activity and molecular weight of a given styrene polymerization catalyst candidate relative to the CSA loading was investigated. The CSAs studied were

10 diethylzinc (DEZ, 25 μmoles or 100 μmoles) and triethylaluminum (TEA, 25 μmoles or 100 μmoles) as models for polymeryl alkylzinc or polymeryl aluminum species, respectively. PPR screening conditions were as follows: [ISOPAR-E + MMAO-3A + T] + (Styrene + CSA + "amines, bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1-) + Catalyst); Catalyst Loading = 0.25 μmoles ; MMAO-3A Loading = 50 μmoles ; T = 75 $^{\circ}\text{C}$ and

15 105 $^{\circ}\text{C}$, t = 15 minutes, [Styrene] = 2.1 M (in toluene).

CAT D was screened in the PPR for its ability to polymerize styrene in the presence of the noted chain shuttling agent. Figure 13 demonstrates that the addition of CSA results in a decrease in the molecular weight, indicating the catalyst participates in effective chain shuttling. CAT D exhibits a relatively low efficiency for styrene polymerization. CAT E

20 was screened in the PPR for its ability to polymerize styrene in the presence of the noted chain shuttling agents. Figure 14 demonstrates that the addition of CSA results in a decrease in the molecular weight, indicating the catalyst participates in effective chain shuttling. CAT E exhibits a relatively low efficiency for styrene polymerization. CAT F was screened in the PPR for its ability to polymerize styrene in the presence of the noted chain shuttling agents.

25 Figure 15 demonstrates that the addition of CSA results in a decrease in the molecular weight, indicating the catalyst participates in effective chain shuttling. CAT F exhibits a relatively low efficiency for styrene polymerization.

CLAIMS

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

- 5 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),

- 10 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;

- 15 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;

- 20 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),

- 25 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_5 - C_{20})aryl group, or a substituted or an unsubstituted (C_5 - C_{20})heteroaryl group;

5 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),

10 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 substituted (C_1 - C_{30})heterohydrocarbyl, or $-H$; and wherein each X is independently a monodentate ligand or a bidentate ligand;

15 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, $-\text{Si}(\text{R}^C)_3$, or $-H$;

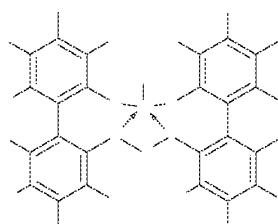
T^1 is selected from $-\text{O}-$, $-\text{S}-$, $-\text{N}(\text{R}^N)-$, or $-\text{P}(\text{R}^P)-$;

t is 1 or 2;

20 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

25 wherein the metal complex is overall charge-neutral;



(Formula S4),

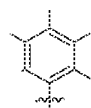
wherein M^1 is a metal selected from zirconium (Zr) or hafnium (Hf); and wherein the metal is in a formal oxidation state of +2, +3, or +4;

each X is independently selected from a substituted or unsubstituted (C_1 - 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;

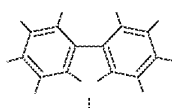
n is 0, 1, or 2, and optionally when n is 1, X may be a bidentate ligand;

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

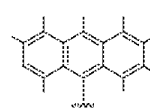
R^6 and R^{21} are each independently selected from the group consisting of -H, a substituted or unsubstituted (C_1 - C_{40})hydrocarbyl, a substituted or unsubstituted (C_1 - C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, 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 - C_{40})hydrocarbyl, a substituted or unsubstituted (C_1 - C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-N=CHR^C$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, halogen, or -H;

each of R^{7-20} is independently selected from a substituted or unsubstituted (C_1 - C_{40})hydrocarbyl, a substituted or unsubstituted (C_1 - C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-N=CHR^C$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, halogen, or -H;

J^4 is a substituted or unsubstituted (C_1 - C_{40})hydrocarbylene or a substituted or unsubstituted (C_1 - C_{40})heterohydrocarbylene, wherein the substituted or unsubstituted (C_1 - 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^{44-51} are each independently selected from a substituted or unsubstituted (C_1-C_{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^{44-51} 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;

5 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;

10 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),

15 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;

20 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;

25 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

5 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

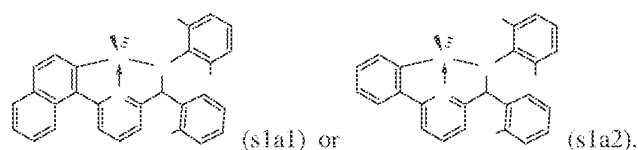
10 wherein if step B occurs before step A, then at least one chain shuttling agent is fed into the reactor B; and

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

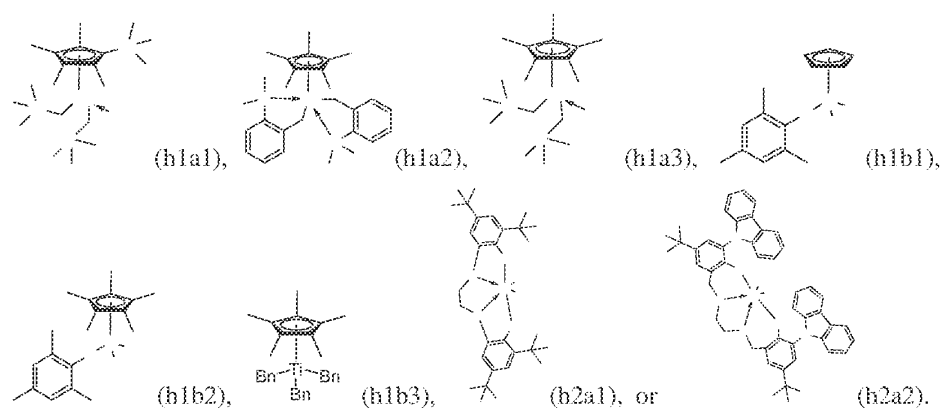
2. The process of claim 1, wherein the metal complex S is selected from Formula S1,

15 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:



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 ($Ph-CH_2-$)):



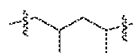
5. The process of any one of claims 1-4, wherein the at least one chain shuttling agent is selected from the following: an alkyl zinc compound, an alkyl aluminum compound, a dual headed chain shuttling agent, or a combination thereof.
6. The process of any one of claims 1-5, wherein step A occurs before step B.
- 5 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 interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, the vinylarene is styrene.
9. The process of any one of claims 1-8, wherein the mixture A comprises the alpha-olefin.
- 10 10. A composition formed from the process of any one of claims 1-9.
11. A composition comprising an ethylene/vinylarene diblock interpolpolymer or an ethylene/vinylarene triblock interpolpolymer, said diblock interpolpolymer comprising at least one polymer structure selected from Structure 1, as shown below, and said triblock interpolpolymer comprising at least one polymer structure selected from Structure 2 or Structure 3, each as
- 15 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,
 - 20 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)
 - 25 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.
12. The composition of claim 11, wherein, for the ethylene/vinylarene diblock
- 30 interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, 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.
13. The composition of claim 11 or claim 12, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, 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.

14. The composition of any one of claims 11-13, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AR) segment
5 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.

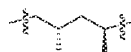
15. The composition of any one of claims 11-14, wherein, for the ethylene/vinylarene diblock interpolpolymer or the ethylene/vinylarene triblock interpolpolymer, each (AP) segment
10 independently comprises, in polymerized form, from 50 mol% to 100 mol% of ethylene, based on the total moles of polymerized monomers in the (AP) segment.

16. The composition of any one of claims 11-15, wherein, for the ethylene/vinylarene diblock interpolpolymer or triblock interpolpolymer, ≥ 20 mol% of the polymerized vinylarene in each (AR) segment is present in a "back to back" configuration as shown below in subsegment bb:



15 (subsegment bb); 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 11-16, wherein, for the ethylene/vinylarene diblock interpolpolymer or triblock interpolpolymer, ≥ 20 mol% of the polymerized vinylarene in each (AR) segment is present in a syndiotactic "back to back" configuration as shown below



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

18. The composition of any one of claims 11-17, wherein, for the ethylene/vinylarene diblock interpolpolymer or triblock interpolpolymer, none of the polymerized vinylarene in each (AP) segment is present in a "back to back" configuration as shown below in subsegment bb:



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

19. The composition of any one of claims 11-18, wherein, for the ethylene/vinylarene diblock interpolpolymer or triblock interpolpolymer, the vinylarene is styrene.

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