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).

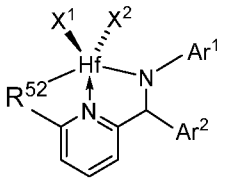
Additional olefin block copolymers (OBCs) and associated polymerizations are disclose in the following references: U.S. Patent 7,915,192; U.S. Patent 8,124,709; U.S. Patent 8,501,885; U.S. Patent 8,716,400; EP1716190B1; EP1926763B1; and EP2582747B1.

However, there remains a need for stereo controlled ethylene/vinylarene multiblock interpolymers, and a need for their preparation using single reactor, continuous solution polymerizations. These needs have been met by the following invention.

SUMMARY OF THE INVENTION

In a first aspect, a process to form a composition comprising an ethylene/vinylarene multiblock interpolymer, said process comprising polymerizing, in a single reactor, a mixture comprising ethylene, a vinylarene, and optionally an alpha-olefin, in the presence of at least the following components *a)-c):*

a) a first metal complex selected from the following Formula A:



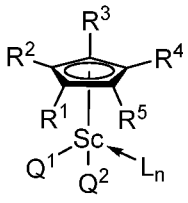
(Formula A),

wherein X^1 and X^2 are each independently selected from a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{30})$heterohydrocarbyl; 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^{52} is a substituted or unsubstituted arylene group;

b) a second metal complex selected from the following Formula B:



(Formula B), 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;

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

c) a chain shuttling agent selected from the following: a dialkyl zinc, a trialkyl aluminum, or a combination thereof.

In a second aspect, a composition comprising an ethylene/vinylarene multiblock interpolymer, said interpolymer comprising at least one polymer structure selected from Structure 1 or Structure 2, each as shown below, and where (AR) refers to a vinylarene rich segment and (AP) refers to a vinylarene poor segment:

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

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

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 1 depicts the ^{1}H NMR profile of CAT B.

Figure 2 depicts the ^{13}C NMR profile of CAT B.

high "back-to-back" vinylarene insertion to generate a syndiotactic configuration; c) had high chain shuttling constants, as determined by molecular weight reduction and narrowing of the molecular weight distribution in the presence of a CSA; d) had high activity in the presence of ethylene; and e) had low alpha-olefin incorporation.

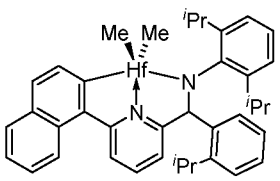
As discussed above, in a first aspect, the invention provides a process to form a composition as discussed above. The inventive process may comprise a combination of two or more embodiments described herein. Each component *a, b* and *c* may each independently comprise a combination of two or more embodiments described herein.

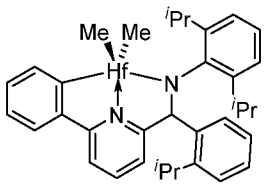
As discussed above, in a second aspect, the invention provides a composition as discussed above. The inventive composition may comprise a combination of two or more embodiments described herein. Structure 1 and Structure 2 may each independently comprise a combination of two or more embodiments described herein.

Note, as used herein, in reference to structures of a metal complex, $X^1 = X1$, $X^2 = X2$, and $Ar1 = Ar^1$, $Ar2 = Ar^2$, $Ar3 = Ar^3$, 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.

The following embodiments apply to an inventive process.

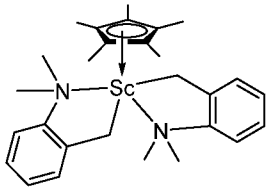
In one embodiment, or a combination of two or more embodiments, each described herein, Formula A is selected from the following structures (a11) or (a12):

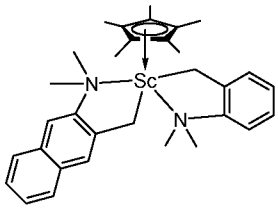


(a11) or


(a12), and further from structure (a11).

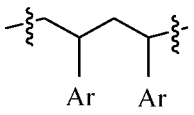
In one embodiment, or a combination of two or more embodiments, each described herein, Formula B is selected from the following structures (b11) or (b12):



(b11) or


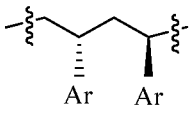
(b12), and further from structure (b11).

In one embodiment, or a combination of two or more embodiments, each described herein, the chain shuttling agent (*component c*) is selected from the following: $Zn(CH_2CH_3)_2$, $Al(CH_2CH_3)_3$, or a combination thereof.



(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, each (AR) segment independently comprises ≤ 100 mol% of the polymerized vinylarene in a "back to back" configuration, as shown in subsegment bb above.

In one embodiment, or a combination of two or more embodiments, each described herein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises ≥ 20 mol% or ≥ 30 mol%, or ≥ 40 mol%, or ≥ 50 mol% or ≥ 60 mol%, or ≥ 70 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 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, each (AR) segment independently comprises ≤ 100 mol% of the polymerized vinylarene in a "back to back" configuration, as shown in subsegment sbb above.

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

In one embodiment, or a combination of two or more embodiments, each described herein, the ethylene/vinylarene multiblock interpolymer is an ethylene/alpha-olefin/vinylarene multiblock interpolymer, and further an ethylene/alpha-olefin/vinylarene multiblock terpolymer.

In one embodiment, or a combination of two or more embodiments, each described herein, the composition further comprises a polyethylene homopolymer, an ethylene/vinylarene copolymer, an ethylene/alpha-olefin copolymer, or a combination thereof.

Also provided is an article comprising at least one component formed from the composition of one or more embodiments described herein.

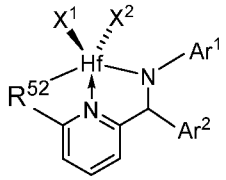
(for example, oxygen). Examples of some scavenger include aluminum alkyl compounds, such as MMAO and MMAO-3A.

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 multiblock interpolymer, said process comprising polymerizing, in a single reactor, a mixture comprising ethylene, a vinylarene, and optionally an alpha-olefin, in the presence of at least the following components *a)-c)*:

a) a first metal complex selected from the following Formula A:



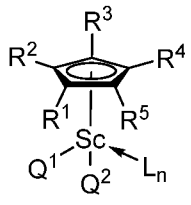
(Formula A),

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, and further a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, and further an alkyl; 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^{52} is a substituted or unsubstituted arylene group;

b) a second metal complex selected from the following Formula B:



(Formula B), 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

heterohydro-carbyl 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

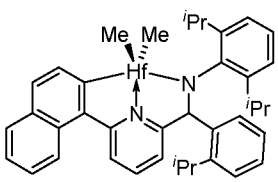
L is a Lewis base; each n is independently 0 or 1; and

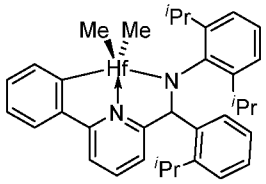
wherein optionally at least one L group and at least one Q group are connected, and optionally at least one R group and at least one Q group are connected;

c) a chain shuttling agent selected from the following: a dialkyl zinc, a trialkyl aluminum, or a combination thereof.

B] The process of A] above, wherein, for Formula A, X^1 and X^2 are each independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, and further an alkyl, and further $X^1 = X^2$.

C] The process of A] or B] above, wherein Formula A is selected from the following structures (a11) or (a12):



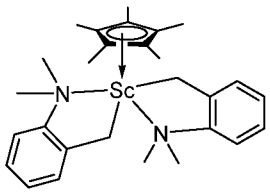
(a11) or


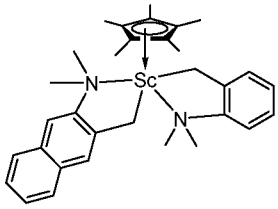
(a12), and further from structure (a11).

D] The process of any one of A]-C] above, wherein, for Formula B, R^1-R^5 are each, independently, H, an alkyl, and further a C_1-C_5 alkyl, further a C_1-C_4 alkyl, further a C_1-C_3 alkyl, further a C_1-C_2 alkyl, further methyl.

E] The process of any one of A]-D] above, wherein, for Formula B, $R^1 = R^2 = R^3 = R^4 = R^5$.

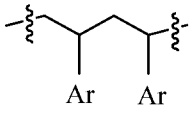
F] The process of any one of A]-E] above, wherein Formula B is selected from the following structures (b11) or (b12):



(b11) or


(b12), and further from structure (b11).

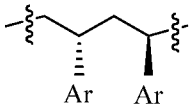
mol%, or ≥ 96 mol%, or ≥ 98 mol%, or ≥ 99 mol% of the polymerized vinylarene in a "back to back" configuration, as shown below in subsegment bb:



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

R2] The process of any one of A]-X] or Q2] above or the composition of any one of A2]-Q2] above, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises ≤ 100 mol% of the polymerized vinylarene in a "back to back" configuration, as shown in subsegment bb above.

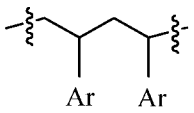
S2] The process of any one of A]-X] or Q2] or R2] above or the composition of any one of A2]-R2] above, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises ≥ 20 mol% or ≥ 30 mol%, or ≥ 40 mol%, or ≥ 50 mol% or ≥ 60 mol%, or ≥ 70 mol%, or ≥ 80 mol%, 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 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.

T2] The process of any one of A]-X] or Q2]-S2] above or the composition of any one of A2]-S2] above, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises ≤ 100 mol% of the polymerized vinylarene in a syndiotactic "back to back" configuration, as shown in subsegment sbb above.

U2] The process of any one of A]-X] or Q2]-T2] above or the composition of any one of A2]-T2] above, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AP) segment independently comprises ≥ 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 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.

V2] The process of any one of A]-X] or Q2]-U2] above or the composition of any one of A2]-U2] above, wherein, for the ethylene/vinylarene multiblock interpolymer, none of the

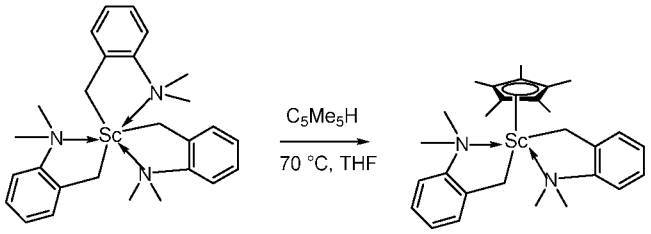
experimental measurement, by sampling the liquid phase and using an online gas chromatograph, or through spectroscopic techniques, such as Fourier-Transform Near-Infrared spectroscopy or Raman spectroscopy. An alternative method is to accurately measure the amount of each reactant and solvent added to the reactor, as well as the temperature and pressure, and then use a thermodynamic "equation of state" model to calculate the amount of liquid and vapor phase present, as well as the composition of each phase. Suitable equations of state include the Redlich-Kwong-Soave [1], Peng–Robinson [2], or more recently, the Perturbed Chain Statistical associating fluid theory PC-SAFT equation of state [3]. Thermodynamic parameters can be obtained from the literature, and the equations solved in a spreadsheet or other computer calculation. Alternatively, commercial process simulation software can be used to solve the chosen equation of state model and determine conditions within the batch reactor. Examples include ASPEN PLUS [4], CHEMCAD [5], or gPROMS [6]. ASPEN PLUS in conjunction with the PC-SAFT equation of state was used in the experimental examples – see Figure 7.

[1] Soave, Giorgio. "Equilibrium constants from a modified Redlich-Kwong equation of state". Chemical Engineering Science. 27 (6): 1197–1203.
[2] Peng, D. Y.; Robinson, D. B. "A New Two-Constant Equation of State". Industrial and Engineering Chemistry: Fundamentals. 15: 59–64.
[3] Gross, Joachim; Sadowski, Gabriele. "Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules". Industrial & Engineering Chemistry Research. 40 (4): 1244–1260.
[4] https://www.aspentech.com/products/engineering/aspen-plus
[5] https://www.chemstations.com/CHEMCAD/
[6] https://www.psenterprise.com/

EXPERIMENTAL

Study 1: Vinylarene-Rich (Hard Block) Analysis

Synthesis of $(C_5Me_5)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$, CAT B



CAT B

In a nitrogen-filled glovebox, a THF solution (1 mL) of $Sc(CH_2CH_6H_4NMe_2\text{-}o)_3$ (0.300 g, 0.67 mmol) was added to a THF solution (1 mL) of C_5Me_5H (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

Additional Studies – CAT B

Figure 4 depicts T_m (from DSC measurements) and the mole percentage of "back to back styrene incorporation" or T_{bb} (as determined by ^{13}C NMR), each as a function of the mole percentage of polymerized (or incorporated) styrene (as determined by ^{13}C NMR). As seen in this figure, as the amount of ethylene (C2) incorporation increases, the Tm of the sPS decreases below the T_m of pure sPS (270 °C), and the mole percentage of T_{bb} also decreases. Samples include the batch reactor samples of Tables 2 and 3.

Figure 5 depicts the weight average molecular weight (M_w) (from GPC) and the T_m (from DSC), each as a function of the noted polymerization parameters. As seen in this figure, the presence of the chain shuttling agents results in a decrease in molecular weight and T_m, indicating the presence of chain shuttling in the reaction mixture. Also, the presence of 1-octene did not significantly impact molecular weight or T_m. Samples were prepared in accordance with the above batch polymerization, and using the conditions shown in Table 4.

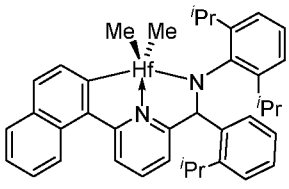
Table 4: Batch Reactor Conditions for Samples in Figure 5

CSA	Initial C2, g	Sty, g	C8, g
None	2.6	60.0	0
None	2.6	60.0	60.0
TEA	2.6	60.0	0
DEZ	2.6	60.0	0

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

The data from Study 1 demonstrate the desirable copolymerization characteristics that the scandium catalyst, CAT B, has for the intended chain shuttling polymerization, which requires this catalyst to make a polystyrene or poly(styrene-co-ethylene) with a high melting temperature, in presence of an alpha-olefin, such as 1-octene. For this scheme to be successful, the catalyst should desirably have a high reactivity towards styrene, but a very low reactivity toward the alpha-olefin. The above tables and figures show a high reactivity for styrene and ethylene, but very low reactivity toward 1-octene. Additionally, the desirable chain shuttling characteristics are maintained, as evidenced by the reduction in molecular weight for polymerizations conducted in presence of DEZ or TEA.

Study 2: Vinylarene-Poor (Soft Block) Analysis

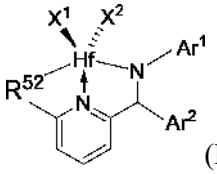


CAT A (See WO03/40195, WO04/24740 and US 8,501,885)

Claims

1. A process to form a composition comprising an ethylene/vinylarene multiblock interpolymer, said process comprising polymerizing, in a single reactor, a mixture comprising ethylene, a vinylarene, and optionally an alpha-olefin, in the presence of at least the following components *a)-c)*:

a) a first metal complex selected from the following Formula A:



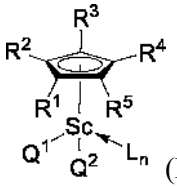
(Formula A),

wherein X^1 and X^2 are each independently selected from a substituted or unsubstituted (C1- C30)hydrocarbyl, a substituted or unsubstituted (C1-C30)heterohydrocarbyl; 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,

R52 is a substituted or unsubstituted arylene group;

b) a second metal complex selected from the following Formula B:



(Formula B), 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;

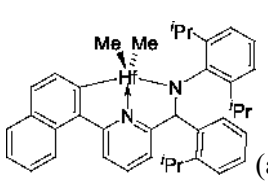
Q1 and Q^2 are each independently a substituted or unsubstituted hydrocarbyl group, or a substituted or unsubstituted heterohydrocarbyl group, or a halogen; and

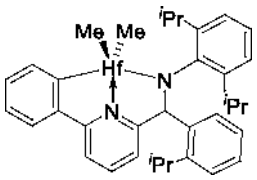
L is a Lewis base; each n is independently 0 or 1; and

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;

c) a chain shuttling agent selected from the following: a dialkyl zinc, a trialkyl aluminum, or a combination thereof.

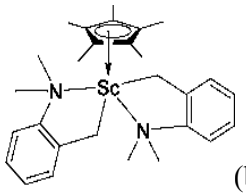
2. The process of claim 1, wherein Formula A is selected from the following structures (a11) or (a12):

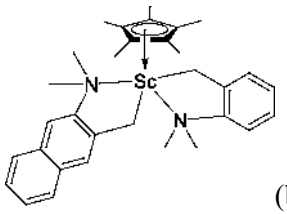


(a11) or 

(a12).

3. The process of claim 1 or claim 2, wherein Formula B is selected from the following structures (b11) or (b12):



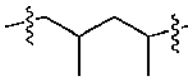
(b11) or 

(b12).

4. The process of any one of claims 1-3, wherein the chain shuttling agent (*component c*) is selected from the following: Zn(CH2CH3)2, Al(CH2CH3)3, or a combination thereof.

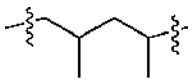
5. The process of any one of claims 1-4, wherein the mixture comprises the alpha-olefin.

6. The process of any one of claims 1-5, wherein the ethylene/vinylarene multiblock interpolymer comprises two or more (AR) segments, and each (AR) segment independently comprises from 20 mol% to 100 mol% of the polymerized vinylarene 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.

7. The process of any one of claims 1-6, wherein the ethylene/vinylarene multiblock interpolymer comprises two or more (AR) segments, and each (AR) segment independently comprises from 20 mol% to 100 mol% of the polymerized vinylarene 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.

8. A composition comprising an ethylene/vinylarene multiblock interpolymer, said interpolymer comprising at least one polymer structure selected from Structure 1 or Structure 2, each as shown below, and where (AR) refers to a vinylarene rich segment and (AP) refers to a vinylarene poor segment:

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

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

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

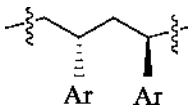
wherein each (AR) segment independently comprises, in polymerized form, > 10 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment; and

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.

9. The composition of claim 8, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises, in polymerized form, from 15 mol% to < 100 mol% of the vinylarene, based on the total moles of polymerized monomers in the (AR) segment.

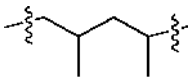
10. The composition of claim 8 or claim 9, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises, in polymerized form, from 2 mol% to 80 mol% of the ethylene, based on the total moles of polymerized monomers in the (AR) segment.

11. The composition of any one of claims 8-10, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises from 20 mol% to 100 mol% of the polymerized vinylarene 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.

12. The composition of any one of claims 8-11, wherein, for the ethylene/vinylarene multiblock interpolymer, each (AR) segment independently comprises from 20 mol% to 100 mol% of the polymerized vinylarene 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.

13. The composition of any one of claims 8-12, wherein composition further comprises a polyethylene homopolymer, an ethylene/vinylarene copolymer, an ethylene/alpha-olefin copolymer, or a combination thereof.

14. An article comprising at least one component formed from the composition of any one of claims 8-13.