COMB ARCHITECTURE OLEFIN BLOCK COPOLYMERS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to US Provisional Application Serial No. 61/388191 filed on September 30, 2010, the contents of which are herein incorporated by reference in their entirety for the purpose of US patent practice.

FIELD OF THE INVENTION

[1] This invention relates to comb architecture olefin block copolymers.

BACKGROUND OF THE INVENTION

[2] Olefin Block Copolymers (OBC) can exhibit a unique balance of flexibility-heat resistance-recovery properties. In particular, the high temperature compression set properties of OBCs with ethylene crystallinity are comparable to or exceed those of the incumbent materials such as f-PVC and SEBS for profile and gasket applications. However, it would be desirable to improve the rheology of these polymers for melt processability of extruded profiles, gaskets, foams etc. Several options have been explored to improve melt rheological behavior of OBCs to allow improved use in extruded profile applications, such as peroxide modification and E-beam crosslinking, such as described in US Patent No. 7,795,321. Branching of OBCs has been disclosed in US Patent Application Publication No. 2009/0163667.

[3] Comb polymers, in general, have been previously described in, for example, "Metallocene-Based Branch–Block Thermoplastic Elastomers" Eric J. Markel, et al, *Macromolecules*, 2000, 33 (23), 8541-8548, "Characterization and Modeling of Metallocene-Based Branch–Block Copolymers" Armenag H. Dekmezian, et al, *Macromolecules*, 2002, 35 (25), 9586-9594, US Patent No. 6,423,793, US Patent No. 6,147,180, and US Patent No. 6,444,773.

[4] It would be advantageous to provide comb architecture olefin block copolymers (C-OBCs) with improved properties.

SUMMARY ~~OF THE INVENTION~~

[5] According to the present disclosure~~invention~~ there is now provided a composition for use in the polymerization of an addition polymerizable monomer, preferably two or more addition polymerizable monomers, especially ethylene and at least one copolymerizable comonomer, to form a segmented copolymer (multi-block copolymer) having a comb architecture, said copolymer containing therein two or more, preferably three or more segments or blocks differing in one or more chemical or physical properties as further disclosed herein, the composition comprising the admixture or reaction product resulting from combining:

(A) a first olefin polymerization catalyst, Catalyst A, having a high comonomer incorporation index and characterized as poor shuttling in the disclosed~~inventive~~ process,

(B) a second olefin polymerization catalyst, Catalyst B, having a low comonomer incorporation index and characterized as good shuttling in the disclosed~~inventive~~ process, and
(C) a chain shuttling agent containing vinyl unsaturation.

[6] In another embodiment of the ~~invention~~disclosure, there is provided a method for selecting an admixture of catalysts (A) and (B) and chain shuttling agent (C) capable of producing multi-block copolymers according to the ~~invention~~disclosure, especially such copolymers comprising ethylene in polymerized form.

[7] In a further embodiment of the present ~~invention~~ disclosure there is provided a process for preparing a comb architecture olefin block copolymer, especially such copolymer comprising ethylene and optionally one or more addition polymerizable monomers other than ethylene, said process comprising contacting ethylene and optionally one or more addition polymerizable monomers other than ethylene under addition polymerization conditions with a composition comprising:
the admixture or reaction product resulting from combining:
(A) a first olefin polymerization catalyst, Catalyst A, having a high comonomer incorporation index and characterized as poor shuttling in the ~~inventive~~disclosed process,
(B) a second olefin polymerization catalyst, Catalyst B, having a low comonomer incorporation index and characterized as good shuttling in the ~~inventive~~ disclosed process, and
(C) a chain shuttling agent containing vinyl unsaturation.

[8] Preferably, the foregoing process takes the form of a continuous solution process for forming comb block copolymers, comprising a soft backbone and hard or crystalline side chains, using multiple catalysts that are incapable of interconversion. That is the catalysts are chemically distinct. Under continuous solution polymerization conditions, the process is ideally suited for polymerization of mixtures of monomers at high monomer conversions. Under these polymerization conditions, shuttling from the chain shuttling agent to Catalyst B becomes advantaged compared to chain growth, and comb block copolymers according to the ~~invention~~ disclosure are formed in high efficiency. The length of the backbone and crystalline side chains may be controlled independently.

[9] In another embodiment of the ~~invention~~disclosure, comb olefin block copolymers are formed having soft backbones and hard or crystalline side chains, preferably by the process comprising contacting ethylene and optionally one or more addition polymerizable monomers other than ethylene under addition polymerization conditions with a composition comprising:
the admixture or reaction product resulting from combining:
(A) a first olefin polymerization catalyst, Catalyst A, having a high comonomer incorporation index and characterized as poor shuttling in the ~~inventive~~ disclosed process,

(B) a second olefin polymerization catalyst, Catalyst B, having a low comonomer incorporation index and characterized as good shuttling in the ~~inventive~~ disclosed process, and

[10] (C) a chain shuttling agent containing vinyl unsaturation.

[11] In yet another embodiment of the disclosure~~invention~~, there are provided functionalized derivatives of the foregoing comb block copolymers.

[12] In a still further embodiment of the present disclosure~~invention~~, there is provided a polymer mixture comprising: (1) an organic or inorganic polymer, preferably a homopolymer of ethylene or of propylene and/or a copolymer of ethylene or propylene and a copolymerizable comonomer, and (2) a comb block copolymer according to the present disclosure~~invention~~ or prepared according to the process of the present dislcosure~~invention~~. In a desirable embodiment component (1) is a matrix polymer comprising high density polyethylene or isotactic polypropylene and component (2) is an elastomeric comb block copolymer. In a preferred embodiment, component (2) comprises occlusions of the matrix polymer formed during compounding of components (1) and (2).

[12a] In a first aspect, there is provided a comb olefin block copolymer comprising a soft copolymer backbone and hard or crystalline side chains wherein: the soft copolymer comprises ethylene and an α-olefin, and has an α-olefin content greater than 5 wt % to 90 wt %, based on the weight of the polymer, the hard or crystalline side chains comprise ethylene in an amount greater than 95 wt %, and the olefin copolymer has a rheology ratio in the range of from 25.7 to 80.

BRIEF DESCRIPTION OF THE DRAWINGS

[13] Figure 1 shows a schematic showing synthesis and architecture of C-OBCs.

[14] Figure 2 shows a comparison of melt rheology of C-OBCs with two comparative OBCs.

[15] Figure 3 shows rheology ratio as a function of melt index for comparative OBCs and C-OBCs.

[16] Figure 4 shows extensional viscosity as a function of time at different strain rates for Example 6.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Definitions

[17] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

[18] The term "comprising" and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed

CLAIMS

1. A composition comprising the admixture or reaction product resulting from combining:

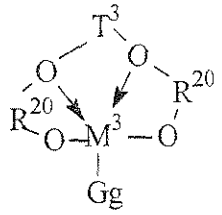
(A) a first olefin polymerization catalyst, Catalyst A, having a high comonomer incorporation index, F1;

(B) a second olefin polymerization catalyst, Catalyst B, having a low comonomer incorporation index, F2; and,

(C) a chain shuttling agent containing vinyl unsaturation;

wherein F1/F2 ≥2 and Catalyst A is a poor shuttler and Catalyst B is a good shuttler.

2. The composition of Claim 1 wherein Catalyst A corresponds to the following formula:



, where:

R^{20} is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

T^3 is a hydrocarbylene or silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

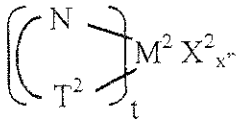
M^3 is a Group 4 metal;

G is an anionic, neutral or dianionic ligand group;

g is a number from 1 to 5 indicating the number of such G groups; and

bonds and electron donative interactions are represented by lines and arrows respectively; and,

wherein Catalyst B corresponds to the following formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

t is one or two;

x" is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

3. The composition of Claim 1 wherein the chain shuttling agent is selected from the group consisting of vinylmethylzinc, (2-propene-1-yl)methylzinc, (2-buten-2-yl)methylzinc, (2-buten-

3-yl)methylzinc, (3-buten-1-yl)methylzinc, (1-butene-2-yl)methylzinc, (1,3-butadiene-1-yl)methylzinc, 1,4-diphenyl-(1,2,3,4-η^4-1,3-butadiene)benzylzinc, di(3-buten-1-yl)zinc, (p-vinylbenzyl)methyl zinc, (7-octenyl)methylzinc, di(7-octenyl)zinc, diallylzinc, (vinyl)ethylzinc, (p-vinylbenzyl)ethylzinc, (vinyl)1-dodecylzinc, (2-propen-1-yl)(trimethylsilylmethyl)zinc, (1,4-butylene)di((2-propen-1-yl)zinc), 5-hexenylzincbromide, (2-propen-1-yl)dimethylaluminum, di(2-propen-1-yl)aluminumbromide, di(5-hexenyl)zinc, 5-hexenylethylzinc, and (5-hexenyl)t-butylzinc.

4. A process for preparing a comb architecture olefin block copolymer comprising contacting ethylene and optionally one or more addition polymerizable monomers other than ethylene under addition polymerization conditions with a composition comprising:

the admixture or reaction product resulting from combining:

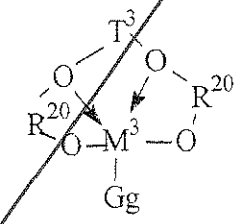
(A) a first olefin polymerization catalyst, Catalyst A, having a high comonomer incorporation index, F1;

(B) a second olefin polymerization catalyst, Catalyst B, having a low comonomer incorporation index, F2; and,

(C) a chain shuttling agent containing vinyl unsaturation;

wherein F1/F2 $\geq$2 and Catalyst A is a poor shuttler and Catalyst B is a good shuttler.

5. The process of Claim 4 wherein Catalyst A corresponds to the following formula:



, where:

R^{20} is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

T^3 is a hydrocarbylene or silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

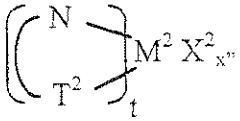
M^3 is a Group 4 metal;

G is an anionic, neutral or dianionic ligand group;

g is a number from 1 to 5 indicating the number of such G groups; and

bonds and electron donative interactions are represented by lines and arrows respectively; and,

wherein Catalyst B corresponds to the following formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

t is one or two;

x" is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

6. The process of Claim 4 wherein the chain shuttling agent is selected from the group consisting of vinylmethylzinc, (2-propene-1-yl)methylzinc, (2-buten-2-yl)methylzinc, (2-buten-3-yl)methylzinc, (3-buten-1-yl)methylzinc, (1-butene-2-yl)methylzinc, (1,3-butadiene-1-yl)methylzinc, 1,4-diphenyl-(1,2,3,4-η^4-1,3-butadiene)benzylzinc, di(3-buten-1-yl)zinc, (p-vinylbenzyl)methyl zinc, (7-octenyl)methylzinc, di(7-octenyl)zinc, diallylzinc, (vinyl)ethylzinc, (p-vinylbenzyl)ethylzinc, (vinyl)1-dodecylzinc, (2-propen-1-yl)(trimethylsilylmethyl)zinc, (1,4-butylene)di((2-propen-1-yl)zinc), 5-hexenylzincbromide, (2-propen-1-yl)dimethylaluminum, di(2-propen-1-yl)aluminumbromide, di(5-hexenyl)zinc, 5-hexenylethylzinc, and (5-hexenyl)t-butylzinc.

7. A comb olefin block copolymer comprising a soft backbone and hard or crystalline side chains wherein the olefin block copolymer has a rheology ratio in the range of from 25.7 to 80.

8. The comb olefin block copolymer of Claim 7 having a melt index, I_2, of from 0.01 to 2000 g/10 min.

9. The comb olefin block copolymer of Claim 7 having side chains present in an amount of from 5 wt% to 50 wt%, based on the weight of the polymer.

10. The comb olefin block copolymer of Claim 7 wherein the backbone has an α-olefin content of greater than 5 wt% to 90 wt% based on the weight of the polymer.

CLAIMS

1. A comb olefin block copolymer comprising a soft copolymer backbone and hard or crystalline side chains wherein:

the soft copolymer comprises ethylene and an α-olefin, and has an α-olefin content greater than 5 wt % to 90 wt %, based on the weight of the polymer,

the hard or crystalline side chains comprise ethylene in an amount greater than 95 wt %, and the olefin copolymer has a rheology ratio in the range of from 25.7 to 80.

2. The comb olefin block copolymer of Claim 1 having a melt index, I_2, of from 0.01 to 2000 g/10 min.

3. The comb olefin block copolymer of Claim 1 having side chains present in an amount of from 5 wt% to 50 wt%, based on the weight of the polymer.

4. The comb olefin block copolymer of Claim 1 wherein the rheology ratio is from 33 to70.

5. The comb olefin block copolymer of Claim 1 wherein the rheology ratio (RR) as a function of melt index (I_2) has the following relationship:

$RR \geqq -11.726\ \mathrm{Ln}(I_2)+36.872$.