PROCESSES FOR THE PRODUCTION OF HIGH MOLECULAR WEIGHT ETHYLENE/ALPHA-OLEFIN/NON-CONJUGATED INTERPOLYMERS WITH LOW LEVELS OF LONG CHAIN BRANCHING

REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Application No. 62/141110, filed March 31, 2015, and incorporated herein by reference.

BACKGROUND

High molecular weight (for example, Mw greater than 150,000 g/mole) ethylene/α-olefin/non-conjugated polyene interpolymers (for example, EPDM terpolymers) with low levels of long chain branching (LCB), as indicated by rheology features (for example, tan delta, V0.1, V100), are useful in many applications, such as TPVs (Thermoplastic Vulcanizates) and high filler compounds. However, production of such high molecular weight interpolymers, in a solution process, has been challenging, for two main reasons: a) the difficulties associated with transporting a high viscosity molten polymer through, and out of, the solution reactors, and b) the need for a catalyst which can produce such high molecular weight interpolymers at commercially viable operating conditions. Thus, there is a need for new polymerization processes to form high molecular weight ethylene/α-olefin/non-conjugated polyene interpolymers with low levels of long chain branching (LCB). This need has been met by the following invention.

SUMMARY

The disclosure provides a process to form a polymer composition comprising at least one ethylene/α-olefin/non-conjugated polyene interpolymer, and wherein the polymer composition has at least the following properties:

a) a Mw/V0.1 ratio greater than, or equal to, 1.80 (g/mol)/(Pa•s);

said process comprising polymerizing one or more mixture(s) comprising ethylene, an α-olefin and a non-conjugated polyene in the presence of a catalyst system comprising a metal-ligand complex of Formula (I):

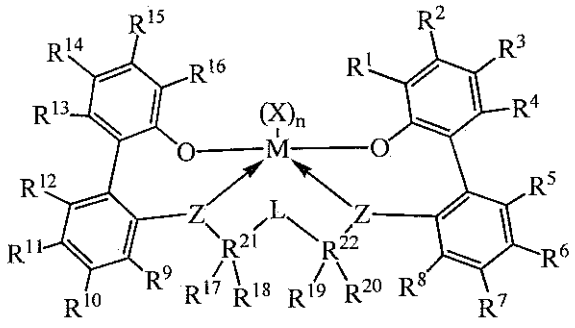
$-N=C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, for Formula I, two or more of R^1 through R^{22}, optionally, may form one or more ring structures, and wherein each ring structure has from 3 to 50 atoms in the ring, excluding any hydrogen atoms.

In one aspect, there is provided a process to form a polymer composition comprising at least one ethylene/α-olefin/non-conjugated polyene interpolymer, and wherein the polymer composition has at least the following properties:

a) a Mw/V0.1 ratio greater than, or equal to, 1.80 (g/mol)/(Pa•s) in the absence of an oil;

said process comprising polymerizing one or more mixture(s) comprising ethylene, an α-olefin and a non-conjugated polyene, in a continuous process and in the presence of a catalyst system comprising a metal-ligand complex of Formula (I):



(Formula I),

wherein:

M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4; and n is an integer of from 0 to 3, and wherein when n is 0, X is absent; and

Each X, independently, is a $(C_1\text{-}C_{40})$hydrocarbyl, a $(C_1\text{-}C_{40})$heterohydrocarbyl , or a halide, and wherein each X, independently, is a monodentate ligand that is neutral, monoanionic, or dianionic; or

wherein two Xs are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic; and

wherein X and n are chosen, in such a way, that the metal-ligand complex of Formula I is, overall, neutral; and

each Z independently is an oxygen atom, a sulfur atom, $-N[(C_1\text{-}C_{40})\text{hydrocarbyl}]-$, or $-P[(C_1\text{-}C_{40})\text{hydrocarbyl}]-$; and

L is a substituted or unsubstituted (C_1-C_{40})hydrocarbylene, or a substituted or unsubstituted (C_1-C_{40})heterohydrocarbylene, and

wherein, for L, the (C_1-C_{40})hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone, linking R^{21} and R^{22} in Formula I (to which L is bonded), or

wherein, for L, the (C_1-C_{40})heterohydrocarbylene has a portion that comprises a 1-atom to 10-atom linker backbone linking R^{21} and R^{22} in Formula I, wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone of the (C_1-C_{40})heterohydrocarbylene, independently, is one of the following: i) a carbon atom, ii) a heteroatom, wherein each heteroatom independently is –O– or –S–, or iii) a substituent selected from -S(O)-, -$S(O)_2$-, -$Si(R^C)_2$-, -$Ge(R^C)_2$-, -$P(R^C)$ -, or -$N(R^C)$-, and 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

R^{21} and R^{22} are each, independently, C or Si; and

R^1 through R^{20} are each, independently, selected from the group consiting of following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, -$Si(R^C)_3$, -$Ge(R^C)_3$, -$P(R^C)_2$, -$N(R^C)_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -$S(O)R^C$, -$S(O)_2R^C$, -$N{=}C(R^C)_2$, -$OC(O)R^C$, -$C(O)OR^C$, -$N(R)C(O)R^C$, -$C(O)N(R^C)_2$, a halogen atom, and a hydrogen atom; and 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, when R^{17} is a hydrogen atom, then R^{18} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, -$Si(R^C)_3$, -$Ge(R^C)_3$, -$P(R^C)_2$, -$N(R^C)_2$, -OR^C, -SR^C, -NO_2, -CN, -CF_3, -$S(O)R^C$, -$S(O)_2R^C$, -$N{=}C(R^C)_2$, -$OC(O)R^C$, -$C(O)OR^C$, -$N(R)C(O)R^C$, -$C(O)N(R^C)_2$, a halogen atom; and 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; or

wherein, when R^{18} is a hydrogen atom, then R^{17} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, -$Si(R^C)_3$,

$-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N=C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen atom; and 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/or

wherein, when R^{19} is a hydrogen atom, then R^{20} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N=C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen atom; and 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; or

wherein, when R^{20} is a hydrogen atom, then R^{19} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N=C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen atom; and 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, for Formula I, two or more of R^1 through R^{22}, optionally, may form one or more ring structures, and wherein each ring structure has from 3 to 50 atoms in the ring, excluding any hydrogen atoms.

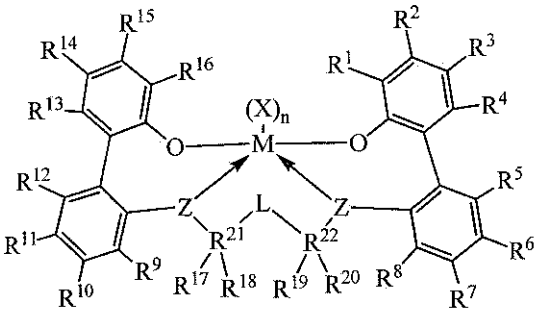
DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that the inventive processes can be used to form ethylene/α-olefin/non-conjugated polyene interpolymers (for example, EPDM terpolymers) with very low levels of long chain branching (LCB). The resulting interpolymers exhibited unique rheological behavior (i.e., high tan delta and low V0.1/V100), enabling such interpolymers to be produced and transported through the devolatilization units and gear pumps, typically used in the solution polymerization processes. These high molecular weight interpolymers can be used to form improved TPV formulations and high filler formulations, each requiring higher performing polymers with improved mechanical properties, and better processability (for example, faster mixing of compounds or improved extrusion processability).

As discussed above, the invention provides a process to form a polymer composition comprising at least one ethylene/α-olefin/non-conjugated polyene interpolymer, and wherein the polymer composition has at least the following properties:

a) a Mw/V0.1 ratio greater than, or equal to, 1.80 (g/mol)/(Pa•s), or greater than, or equal to, 1.85 (g/mol)/(Pa•s), or greater than, or equal to, 1.90 (g/mol)/(Pa•s), or greater than, or equal to, 1.95 (g/mol)/(Pa•s), or greater than, or equal to, 2.00 (g/mol)/(Pa•s);

said process comprising polymerizing one or more mixture(s) comprising ethylene, an α-olefin and a non-conjugated polyene in the presence of a catalyst system comprising a metal-ligand complex of Formula (I):



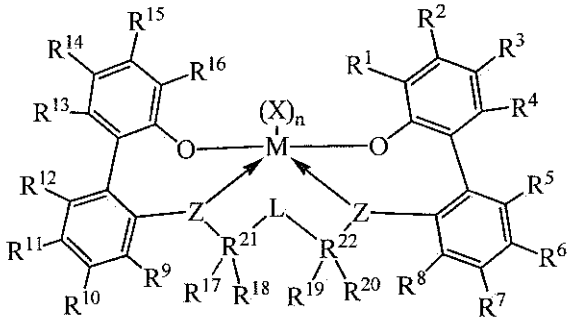
(Formula I), as described herein. Here the Mw is the Mw (conv gpc).

CLAIMS

1. A process to form a polymer composition comprising at least one ethylene/α-olefin/non-conjugated polyene interpolymer, and wherein the polymer composition has at least the following properties:

a) a Mw/V0.1 ratio greater than, or equal to, 1.80 (g/mol)/(Pa•s) in the absence of an oil;

said process comprising polymerizing one or more mixture(s) comprising ethylene, an α-olefin and a non-conjugated polyene, in a continuous process and in the presence of a catalyst system comprising a metal-ligand complex of Formula (I):



(Formula I),

wherein:

M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4; and n is an integer of from 0 to 3, and wherein when n is 0, X is absent; and

Each X, independently, is a $(C_1\text{-}C_{40})$hydrocarbyl, a $(C_1\text{-}C_{40})$heterohydrocarbyl , or a halide, and wherein each X, independently, is a monodentate ligand that is neutral, monoanionic, or dianionic; or

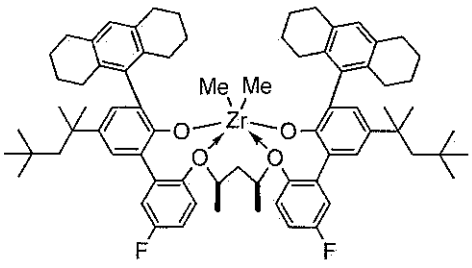
wherein two Xs are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic; and

wherein X and n are chosen, in such a way, that the metal-ligand complex of Formula I is, overall, neutral; and

each Z independently is an oxygen atom, a sulfur atom, -N[$(C_1\text{-}C_{40})$hydrocarbyl]-, or -P[$(C_1\text{-}C_{40})$hydrocarbyl]-; and

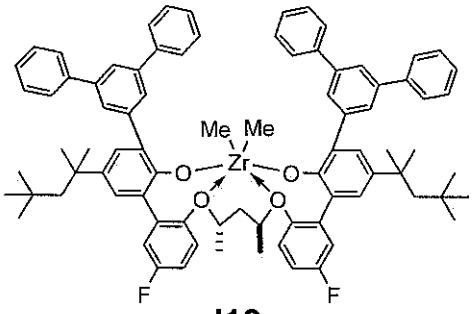
L is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbylene, or a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbylene, and

wherein, for L, the $(C_1\text{-}C_{40})$hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone, linking R^{21} and R^{22} in Formula I (to which L is bonded), or



I11

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I12

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