TELECHELIC POLYOLEFINS AND PROCESSES FOR PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority to U.S. provisional application no. 62/786084, filed on December 28, 2018, which is incorporated herein by reference in its entirety.

FIELD

[0002] Embodiments relate to telechelic polyolefins and processes for preparing the same.

BACKGROUND

[0003] Polyolefins are one of the most important and widely used polymeric materials in the world. Due to their inherent chemical inertness, the introduction of reactive functional groups to form telechelic polyolefins having two reactive end groups has been actively pursued for many years. However, there is a need in the art for a commercially viable process to prepare telechelic polyolefins. The present disclosure addresses such a need and also relates to novel telechelic polyolefin compositions.

SUMMARY

[0004] The present disclosure relates to a composition comprising a telechelic polyolefin of the formula (I):

$A^1L^1L^2A^2$ (I), wherein:

L^1 is a polyolefin;

A^1 is selected from the group consisting of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, a mixture of a vinylidene group of the formula $CH_2=C(Y^1)–$ and a vinylene group of the formula $Y^1CH=CH–$, and a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$;

Y^1 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group;

L^2 is a C_1 to C_{32} hydrocarbylene group; and

A^2 is a hydrocarbyl group comprising a hindered double bond.

[004a] In one aspect, the present disclosure relates to a telechelic polyolefin of the formula (I):

$A^1L^1L^2A^2$ (I), wherein:

L^1 is a polyolefin, wherein L^1 is an ethylene-based polymer;

A^1 is selected from the group consisting of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, a mixture of a vinylidene group of the formula $CH_2=C(Y^1)–$ and a vinylene group of the formula $Y^1CH=CH–$, and a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$;

Y^1 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group;

L^2 is a C_1 to C_{32} hydrocarbylene group; and

A^2 is a hydrocarbyl group comprising a hindered double bond.

[0004b] In another aspect, the present disclosure relates to a composition comprising the telechilic polyolefin as described herein.

[0005] The present disclosure further relates to a process for preparing a composition comprising a telechelic polyolefin, the process comprising:

1) combining starting materials comprising (A) a monomer component, (B) a chain transfer agent component, and (C) a catalyst component to form a solution and polymerizing from greater than 10 mol% to less than or equal to 99 mol% of the (A) monomer component in the solution;

2) heating the solution; and

3) recovering a product comprising the composition comprising the telechelic polyolefin, wherein:

the (B) chain transfer agent component comprises an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$;

Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and

A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

[0005a] In another aspect, the present disclosure relates to a process for preparing a telechelic polyolefin, the process comprising:

1) combining starting materials comprising (A) a monomer component, (B) a chain transfer agent component, and (C) a catalyst component comprising a procatalyst to form a solution and polymerizing from greater than 10 mol% to less than or equal to 99 mol% of the (A) monomer component in the solution;

2) heating the solution; and

3) recovering a product comprising the telechelic polyolefin, wherein:

the (B) chain transfer agent component comprises an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$;

Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and

A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIGS. 1A and 1B provide the 1H NMR and GC/MS spectra for the synthesis of CTA 1, respectively.

[0007] FIG. 2 provides the 1H NMR spectrum for the synthesis of CTA 2.

[0008] FIG. 3 provides the 1H NMR spectrum for the synthesis of a telechelic polyolefin using CTA 7.

[0009] FIG. 4 provides the 1H NMR spectrum for the synthesis of a telechelic polyolefin using CTA 8.

DETAILED DESCRIPTION

Definitions

[0010] 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

What is claimed is:

1. A telechelic polyolefin of the formula (I):

$A^1L^1L^2A^2$ (I), wherein:

L^1 is a polyolefin, wherein L^1 is an ethylene-based polymer;

A^1 is selected from the group consisting of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, a mixture of a vinylidene group of the formula $CH_2=C(Y^1)–$ and a vinylene group of the formula $Y^1CH=CH–$, and a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$;

Y^1 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group;

L^2 is a C_1 to C_{32} hydrocarbylene group; and

A^2 is a hydrocarbyl group comprising a hindered double bond.

~~2. The telechelic polyolefin of claim 1, wherein L^1 is an ethylene-based polymer.~~

~~3.~~2. The telechelic polyolefin of claim 1 ~~or 2~~, wherein L^1 is an ethylene homopolymer or an ethylene/alpha-olefin copolymer comprising units derived from ethylene and a C_3 to C_{30} alpha-olefin.

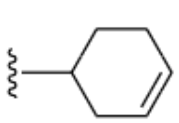
~~4.~~3. The telechelic polyolefin of claim ~~3~~2, wherein the C_3 to C_{30} alpha-olefin is selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene.

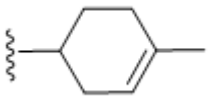
~~5.~~4. The telechelic polyolefin of any of the preceding claims, wherein the hindered double bond is selected from the group consisting of the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.

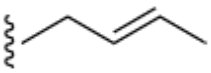
~~6.~~5. The telechelic polyolefin of any of the preceding claims, wherein A^2 is a C_3 to C_{30} cyclic hydrocarbyl group or a C_3 to C_{30} acyclic hydrocarbyl group.

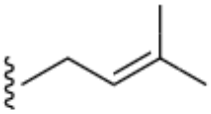
~~7.~~6. The telechelic polyolefin of any of the preceding claims, wherein A^2 is selected from the group consisting of an unsubstituted cycloalkene, an alkyl-substituted cycloalkene, and an acyclic alkyl group.

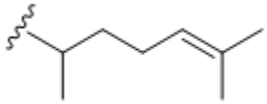
~~8.~~7. The telechelic polyolefin of any of the preceding claims, wherein A^2 is selected from the group consisting of:

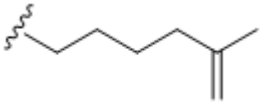

(AC)

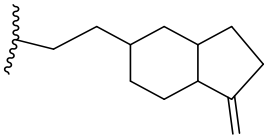

(AF)


(AM)


(AO)


(AP)


(AS)


(AZ1),

wherein the endocyclic double bond in (AC) and (AF) may be between any two adjacent carbon atoms that are ring members, and wherein the pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

~~9.~~8. The telechelic polyolefin of any of the previous claims, wherein the telechelic polyolefin of the formula (I) comprises a weight average molecular weight (Mw) range from 1,000 to 1,000,000 g/mol.

~~10.~~9. The telechelic polyolefin of any of the previous claims, wherein L^1 is covalently bonded to each of A^1 and L^2 through carbon-carbon single bonds, and wherein L^2 is covalently bonded to A^2 through a carbon-carbon single bond.

~~11.~~10. A composition comprising the telechelic polyolefin of any of the previous claims.

~~12.~~11. A process for preparing a telechelic polyolefin, the process comprising:

1) combining starting materials comprising (A) a monomer component, (B) a chain transfer agent component, and (C) a catalyst component comprising a procatalyst to form a

solution and polymerizing from greater than 10 mol% to less than or equal to 99 mol% of the (A) monomer component in the solution;

2) heating the solution; and

3) recovering a product comprising the telechelic polyolefin, wherein:

the (B) chain transfer agent component comprises an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$;

Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and

A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

~~13.~~12. The process of claim ~~12~~11, wherein the starting materials further comprise (D) a solvent.

~~14.~~13. The process of claim ~~12~~11 or ~~13~~12, wherein step 2) is heating the solution to a temperature of at least 160°C and holding the solution at the temperature of at least 160°C for a time of at least 30 seconds.