CATALYST SYSTEM FOR THE PRODUCTION OF POLYOLEFINS AND METHOD OF MAKING AND USING SAME

Field

[0001] The present invention is generally related to the field of polyolefin synthesis, and more particularly, compositions and catalyst systems for the polymerization of olefins.

Background

[0002] Commercially, polyolefins are synthesized using Ziegler-Natta polymerization catalyst systems. These systems typically include a chemical species with a transition metal component and halide components, along with an optional internal electron donor. Additionally, these systems may include a co-catalyst, one or more selectivity control agents (SCA), and one or more activity limiting agents (ALA). Certain SCA and ALA, as well as their functionality in polymerization systems, were described in U.S. Patent No. 7,491,670, the contents of which is incorporated herein by reference.

[0003] In many applications, low volatile organic compound (VOC) levels are preferred, and in some instances, mandated by various governmental bodies. Indeed, high VOC levels are disfavored for health, organoleptic, and environmental reasons. However, many known ALA constituents and their decomposition products may be contained in the final polyolefin product, may contribute to the VOC levels of that final product, and have traditionally been difficult to purge from the final product before it is used in consumer goods.

[0004] Therefore, a need exists for a polymerization catalyst system that minimizes the introduction of VOCs.

Summary

[0005] In an attempt to overcome the noted deficiencies, aspects of the present disclosure are directed toward catalyst systems for polymerization of mixtures comprising an olefin.

[0006] The present disclosure is premised on the realization that lower VOC values are obtainable using certain low carbon-containing esters as ALAs in olefin polymerization catalyst systems. A first aspect of the disclosure is directed to compositions for use with a catalyst for polymerization of mixtures comprising an olefin. The composition includes a selectivity control agent comprising at least one silicon-containing compound containing at least one C1-C10 alkoxy group bonded to a silicon atom and an amount of one or more activity limiting agents

, said activity limiting agents comprising C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0007] The same or a different aspect is directed toward catalyst compositions for polymerization of mixtures comprising an olefin. The catalyst composition includes one or more polymerization catalysts, a selectivity control agent comprising at least one silicon-containing compound containing at least one C1-C10 alkoxy group bonded to a silicon atom, and an amount of one or more activity limiting agents, said activity limiting agents comprising C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0008] A further aspect of the disclosure is directed to a polymerization process. The process includes contacting an olefin or a mixture of the olefin and one or more copolymerizable comonomers under polymerization conditions with a catalyst system that includes one or more polymerization catalysts, a selectivity control agent comprising at least one silicon-containing compound containing at least one C1-C10 alkoxy group bonded to a silicon atom, and an amount of one or more agent compounds, said agent compound comprising C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0008a] In another aspect of the disclosure, there is provided a composition comprising a propylene homopolymer and a C2-C13 mono- or polycarboxylic ester of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0008b] In yet another aspect of the disclosure, there is provided a polymerization process for producing a propylene-based polymer comprising contacting, under polymerization conditions and in the presence of hydrogen, propylene and optionally one or more comonomers with a catalyst composition described herein; maintaining a H_2/propylene mole ratio from 0.0005 to about 0.17 during the contacting; and forming a propylene-based polymer having a melt flow rate from 0.2 g/10 min to 400 g/10 min, as measured in accordance with ASTM D-1238-01 at 230 °C with a 2.16 kg weight of propylene based polymers.

[0008c] In another aspect of the disclosure, there is provided a propylene impact copolymer composition comprising a propylene based polymer; a propylene/ethylene copolymer dispersed within the propylene-based polymer; and a C2-C13 mono- or polycarboxylic ester of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0008d] In a further aspect of the disclosure, there is provided a polymerization process comprising contacting, under polymerization conditions, propylene with a catalyst

composition comprising a C2-C13 mono- or polycarboxylic ester of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof in a first polymerization reactor; forming an active propylene-based polymer contacting, under polymerization conditions, the active propylene-based polymer with at least one olefin in a second polymerization reactor; and forming the composition described herein.

[0008e] In another aspect of the disclosure, there is provided an article comprising a polypropylene homopolymer comprising a C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0008f] In yet another aspect of the disclosure, there is provided an article comprising a polypropylene impact copolymer comprising one or more C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

[0009] The objects and advantages of the present disclosure will be further appreciated in light of the following detailed description and drawings provided herein.

Detailed Description

[0010] Unless clearly defined otherwise from the context, any range of values presented in the following Detailed Description and Claims includes each end point as well as each whole number or fractional part thereof, within the recited range. Additionally, approximating language may be applied to modify any quantitative representation that may vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as “about” and “substantially,” may not be limited to the precise value specified.

[0011] All references to the Periodic Table of the Elements refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2001. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. 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

What is claimed is:

1. A composition for use with a catalyst for polymerization of mixtures comprising an olefin, said composition comprising:

a selectivity control agent comprising at least one silicon-containing compound containing at least one C1-C10 alkoxy group bonded to a silicon atom; and

an amount of one or more activity limiting agents, said activity limiting agents comprising C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

2. The composition of claim 1, wherein:

the amount of said activity limiting agents provides a normalized polymerization activity at a first temperature of 100 °C that is less than one of:

a normalized polymerization activity at a second temperature, said second temperature being 72 °C; or

a normalized polymerization activity at the first temperature in the presence of the selectivity control agent, but not the activity limiting agent, at a same total molar quantity of the selectivity control agent; or

a normalized polymerization activity at the first temperature in the presence of the selectivity control agent, but not the activity limiting agent, at a molar quantity of the selectivity control agent required to produce similar xylene solubles at the second temperature as said composition at the second temperature.

3. The composition of claim 1, wherein the activity limiting agent increases a lifetime of the catalyst during the polymerization of mixtures comprising an olefin.

4. The composition of claim 1, wherein the activity limiting agent comprises an acetate or valerate ester.

5. The composition of claim 1, wherein the activity limiting agent comprises a hexanoate ester.

6. The composition of claim 1, wherein the selectivity control agent comprises *n*-propyltrimethoxysilane.

7. The composition of claim 1, wherein the activity limiting agent comprises a compound selected from the group consisting of butyl valerate, isobutyl butyrate, propyl butyrate, pentyl valerate, isopropyl butyrate, octyl acetate, pentyl acetate, propyl acetate, and combinations thereof.

8. The composition of claim 1, wherein the total quantity of the selectivity control agent is limited to provide a molar ratio, based on the moles of a transition metal in a polymerization catalyst, from 0.1 to 500.

9. The composition of claim 1, wherein the molar ratio of the selectivity control agent to the agent compound is from 99:1 to 0.1 to 99.9.

10. A catalyst composition for polymerization of mixtures comprising an olefin, said catalyst composition comprising:

one or more polymerization catalysts;

a selectivity control agent comprising at least one silicon-containing compound containing at least one C1-C10 alkoxy group bonded to a silicon atom;

an amount of one or more activity limiting agents, said activity limiting agents comprising C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 monocarboxylic acids and inertly substituted derivatives thereof.

11. The catalyst composition of claim 10, wherein:

the amount of said activity limiting agents provides a normalized polymerization activity at a first temperature of 100 °C that is less than one of:

a normalized polymerization activity at a second temperature, said second temperature being 72 °C; or

a normalized polymerization activity at the first temperature in the presence of the selectivity control agent, but not the activity limiting agent, at a same total molar quantity of the selectivity control agent; or

a normalized polymerization activity at the first temperature in the presence of the selectivity control agent, but not the activity limiting agent, at a molar quantity of the selectivity control agent required to produce similar xylene solubles at the second temperature as said catalyst composition at the second temperature.

12. The composition of claim 10, wherein the activity limiting agent increases a lifetime of the catalyst during the polymerization of mixtures comprising an olefin.

13. The composition of claim 10, wherein the activity limiting agent comprises an acetate or valerate ester.

14. The composition of claim 10, wherein the activity limiting agent comprises a hexanoate ester.

15. The composition of claim 10, wherein the selectivity control agent comprises *n*-propyltrimethoxysilane.

16. The composition of claim 10, wherein the activity limiting agent comprises a compound selected from the group consisting of butyl valerate, isobutyl butyrate, propyl butyrate, pentyl valerate, isopropyl butyrate, octyl acetate, pentyl acetate, propyl acetate, and combinations thereof.

17. The composition of claim 10, wherein the polymerization catalyst comprises an aluminum-containing compound.

18. The composition of claim 10, wherein the total quantity of the selectivity control agent is limited to provide a molar ratio, based on the moles of a transition metal in the polymerization catalyst, from 0.1 to 500.

19. The composition of claim 10, wherein the molar ratio of the selectivity control agent to the agent compound is from 99:1 to 0.1 to 99.9.

20. A polymerization process comprising:

contacting an olefin or a mixture of the olefin and one or more copolymerizable comonomers under polymerization conditions with the catalyst composition of claim 10.

21. A composition comprising a propylene homopolymer and a C2-C13 mono- or polycarboxylic ester of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

22. The composition of claim 21, wherein the composition has a melt flow greater than 100 g/10 min, as measured in accordance with ASTM D-1238-01 at 230 °C with a 2.16 kg weight of propylene based polymers.

23. The composition of claim 21, wherein the composition has a VOC content less than 80 ppm, as measured in accordance with VW standard PV 3341.

24. The composition of claim 21, wherein the composition has a VOC content less than 25 ppm, as measured in accordance with VW standard PV 3341, and a melt flow less than 10 g/10 min, as measured in accordance with ASTM D-1238-01 at 230 °C with a 2.16 kg weight of propylene based polymers.

25. A process for producing the composition of claim 21.

26. A polymerization process for producing a propylene-based polymer comprising:

contacting, under polymerization conditions and in the presence of hydrogen, propylene and optionally one or more comonomers with a catalyst composition as claimed in claim 10,

maintaining a H_2/propylene mole ratio from 0.0005 to about 0.17 during the contacting; and

forming a propylene-based polymer having a melt flow rate from 0.2 g/10 min to 400 g/10 min, as measured in accordance with ASTM D-1238-01 at 230 °C with a 2.16 kg weight of propylene based polymers.

27. A propylene impact copolymer composition comprising:

a propylene based polymer;

a propylene/ethylene copolymer dispersed within the propylene-based polymer; and

a C2-C13 mono- or polycarboxylic ester of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

28. The composition of claim 27, wherein the composition has a melt flow greater than 50 g/10 min, as measured in accordance with ASTM D-1238-01 at 230 °C with a 2.16 kg weight of propylene based polymers.

29. The composition of claim 27, wherein the composition has a VOC content less than 30 ppm, as measured in accordance with VW standard PV 3341.

30. A polymerization process comprising:

contacting, under polymerization conditions, propylene with a catalyst composition comprising a C2-C13 mono- or polycarboxylic ester of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof in a first polymerization reactor;

forming an active propylene-based polymer;

contacting, under polymerization conditions, the active propylene-based polymer with at least one olefin in a second polymerization reactor; and

forming the composition of claim 27.

31. An article comprising a polypropylene homopolymer comprising a C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.

32. An article comprising a polypropylene impact copolymer comprising one or more C2-C13 mono- or polycarboxylic esters of aliphatic C2-C7 carboxylic acids and inertly substituted derivatives thereof.