composition made thereby always contains some amount of both the LMW polyethylene component and the HMW polyethylene component.

[0009] Further, transitions between bimodal catalyst systems ("catalyst transitions") such as between different precatalysts or between different amounts of a same precatalyst in the single polymerization reactor are complex. For example, it is complex to transition from a first bimodal catalyst system comprising a first MCN catalyst (abbreviated LMW-CAT-1) and a first insoluble non-MCN precatalyst to a second bimodal catalyst system comprising a second MCN catalyst (abbreviated LMW-CAT-2) and the same first insoluble non-MCN precatalyst, wherein LMW-CAT-1 and LMW-CAT-2 are different from each other and from the insoluble non-MCN precatalyst. Even though the insoluble non-MCN precatalyst is the same in the first parts of both the first and second bimodal catalyst systems, both the first and second parts of the first bimodal catalyst system must be replaced in order to transition to the second bimodal catalyst system. This is because both the first and second parts contain the no longer wanted LMW-CAT-1 component.

[0010] Also, certain insoluble non-MCN precatalysts become unstable after being mixed with the activator. It is necessary to chill those first parts (containing unstable/insoluble non-MCN precatalyst) of the bimodal catalyst system to about -10 degrees Celsius (° C.) for shipment or storage thereof. Then, the second part may need to be reformulated to withstand cooling "shock" when it contacts the chilled first part in the in-line mixer. Or the first part may need to be warmed before being fed into the in-line mixer.

[0011] And because insoluble non-MCN precatalyst is insoluble in alkanes, it is not suitable for use in the second part (trim catalyst) in the combining-the-parts feed method.

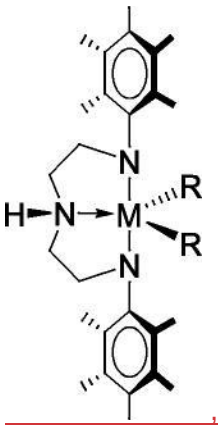
SUMMARY

[0012] A method of polymerizing an olefin monomer to make a polyolefin composition, the method comprising contacting a solution of an alkane-soluble non-metallocene precatalyst dissolved in an alkane solvent with an activator so as to make a trim catalyst comprising an alkane-soluble non-metallocene catalyst, feeding the trim catalyst, as a solution in an alkane solvent or supported on a support material as a dry powder or a slurry thereof in an alkane solvent, into a polymerization reactor, and polymerizing the olefin monomer with the trim catalyst in the polymerization reactor, thereby making the polyolefin composition.

[0012a] In one aspect, the present disclosure refers to a method of polymerizing an olefin monomer to make a first polyolefin composition comprising a first polyolefin polymer, the method comprising steps (A) to (C): (A) contacting a solution of a first alkane-soluble non-metallocene precatalyst dissolved in an alkane solvent with an activator so as to make a first trim catalyst comprising a first alkane-soluble non-metallocene catalyst; (B) feeding the first trim catalyst into a polymerization reactor; and (C) polymerizing the olefin monomer with the first trim catalyst in the polymerization reactor; thereby making the first polyolefin composition

comprising the first polyolefin polymer; wherein the first alkane-soluble non-metallocene precatalyst is characterized by solubility in hexanes containing at least 60 weight percent n-hexane of at least 0.10 weight percent, based on total weight of the first alkane-soluble non-metallocene precatalyst and hexanes, measured using Solubility Test Method;

wherein the alkane-soluble non-metallocene precatalyst is a compound of formula (1):



(1)

wherein M is a Group 4 metal and each R is independently selected from a silicon-free organic solubilizing group;

wherein each R that is independently selected from a silicon-free organic solubilizing group is independently methyl, an unsubstituted (C_2-C_4)alkyl group, an unsubstituted (C_5-C_{12})alkyl group, an unsubstituted or substituted quaternary-arylalkyl group; or both R groups are bonded together to give R′-R′, wherein R′-R′ is an unsubstituted or substituted (aryl)alkylene;

wherein each R group and R′-R′ group is free of a cyclopentadienyl group, a silicon atom, a carbon-carbon double bond, and a carbon-carbon triple bond;

wherein each substituent independently may be selected from unsubstituted (C_1-C_5)alkyl, halogen, -Oalkyl, and -N(alkyl)$_2$;

wherein each quaternary-arylalkyl group sequentially contains a quaternary alkyl, a phenylene, and a (C_1-C_3)alkylene linker, wherein the quaternary alkyl is bonded to the phenylene, which is bonded to the (C_1-C_3)alkylene linker, which is bonded to the metal M;

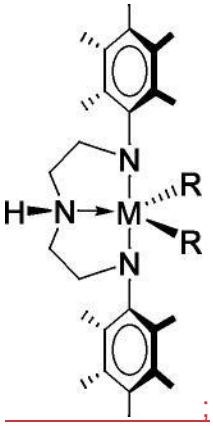
wherein the (C_1-C_3)alkylene linker and R′-R′ groups are divalent; and

wherein the quaternary alkyl contains a quaternary carbon atom, which may be directly or indirectly bonded to the phenylene, wherein the quaternary carbon atom is an element having atomic number 6 in the Periodic Table of the Elements that is bonded to four other carbon atoms.

[0012b] In another aspect, the present disclosure refers to a method of polymerizing an olefin monomer to make a first bimodal polyolefin composition comprising a first higher molecular

weight (HMW) polyolefin component and a first lower molecular weight (LMW) polyolefin component, the method comprising steps (1) to (5): (1) contacting a solution of a first alkane-soluble non-metallocene precatalyst dissolved in an alkane solvent with an activator so as to make a first trim catalyst comprising a first alkane-soluble non-metallocene catalyst; (2) contacting a first metallocene precatalyst and an additional amount of the first alkane-soluble non-metallocene precatalyst with an activator and, optionally, a support material so as to make a first bimodal catalyst system comprising a first metallocene catalyst and an additional amount of the first alkane-soluble non-metallocene catalyst, optionally free of the support material or disposed on and/or in the support material; (3) contacting the first bimodal catalyst system with the first trim catalyst to make a first mixed catalyst system comprising a mixture of the first bimodal catalyst system and the first trim catalyst; (4) feeding the first mixed catalyst system into a polymerization reactor; and (5) polymerizing the olefin monomer with the first mixed catalyst system in the polymerization reactor; thereby making the first HMW polyolefin component and the first LMW polyolefin component of the first bimodal polyolefin composition; wherein the first ASNM Precatalyst is characterized by solubility in hexanes containing at least 60 weight percent n-hexane of at least 0.10 weight percent based on total weight of the first ASNM Precatalyst and hexanes, as measured using Solubility Test Method;

wherein the alkane-soluble non-metallocene precatalyst is a compound of formula (1):



(1)

;

wherein M is a Group 4 metal and each R is independently selected from a silicon-free organic solubilizing group;

wherein each R that is independently selected from a silicon-free organic solubilizing group is independently methyl, an unsubstituted (C_2-C_4)alkyl group, an unsubstituted (C_5-C_{12})alkyl group, an unsubstituted or substituted quaternary-arylalkyl group; or both R groups are bonded together to give R′-R′, wherein R′-R′ is an unsubstituted or substituted (aryl)alkylene;

wherein each R group and R′-R′ group is free of a cyclopentadienyl group, a silicon atom, a carbon-carbon double bond, and a carbon-carbon triple bond;

wherein each substituent independently may be selected from unsubstituted (C_1-C_5)alkyl, halogen, -Oalkyl, and -N(alkyl)$_2$;

wherein each quaternary-arylalkyl group sequentially contains a quaternary alkyl, a phenylene, and a (C_1-C_3)alkylene linker, wherein the quaternary alkyl is bonded to the phenylene, which is bonded to the (C_1-C_3)alkylene linker, which is bonded to the metal M;

wherein the (C_1-C_3)alkylene linker and R′-R′ groups are divalent; and

wherein the quaternary alkyl contains a quaternary carbon atom, which may be directly or indirectly bonded to the phenylene, wherein the quaternary carbon atom is an element having atomic number 6 in the Periodic Table of the Elements that is bonded to four other carbon atoms.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure (Fig.) 1 is a Gel Permeation Chromatogram (GPC) of a bimodal polyethylene composition made according to the method of Inventive Example 9A.

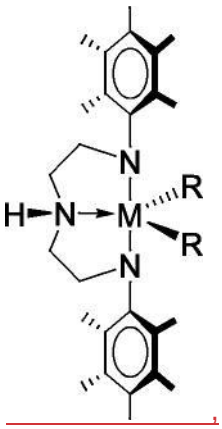
[0014] Fig. 2 contains structural formulas of some embodiments of the alkane-soluble non-metallocene precatalyst.

[0015] Fig. 3 contains structural formulas of some embodiments of intermediates useful in synthesizing the embodiments of the alkane-soluble non-metallocene precatalysts of Fig. 2.

CLAIMS

1. A method of polymerizing an olefin monomer to make a first polyolefin composition comprising a first polyolefin polymer, the method comprising steps (A) to (C): (A) contacting a solution of a first alkane-soluble non-metallocene precatalyst dissolved in an alkane solvent with an activator so as to make a first trim catalyst comprising a first alkane-soluble non-metallocene catalyst; (B) feeding the first trim catalyst into a polymerization reactor; and (C) polymerizing the olefin monomer with the first trim catalyst in the polymerization reactor; thereby making the first polyolefin composition comprising the first polyolefin polymer; wherein the first alkane-soluble non-metallocene precatalyst is characterized by solubility in hexanes containing at least 60 weight percent n-hexane of at least 0.10 weight percent, based on total weight of the first alkane-soluble non-metallocene precatalyst and hexanes, measured using Solubility Test Method;

wherein the alkane-soluble non-metallocene precatalyst is a compound of formula (1):



(1)

,

wherein M is a Group 4 metal and each R is independently selected from a silicon-free organic solubilizing group;

wherein each R that is independently selected from a silicon-free organic solubilizing group is independently methyl, an unsubstituted (C_2-C_4)alkyl group, an unsubstituted (C_5-C_{12})alkyl group, an unsubstituted or substituted quaternary-arylalkyl group; or both R groups are bonded together to give R′-R′, wherein R′-R′ is an unsubstituted or substituted (aryl)alkylene;

wherein each R group and R′-R′ group is free of a cyclopentadienyl group, a silicon atom, a carbon-carbon double bond, and a carbon-carbon triple bond;

wherein each substituent independently may be selected from unsubstituted (C_1-C_5)alkyl, halogen, -Oalkyl, and -N(alkyl)$_2$;

wherein each quaternary-arylalkyl group sequentially contains a quaternary alkyl, a phenylene, and a (C_1-C_3)alkylene linker, wherein the quaternary alkyl is bonded to the phenylene, which is bonded to the (C_1-C_3)alkylene linker, which is bonded to the metal M;

wherein the (C_1-C_3)alkylene linker and R′-R′ groups are divalent; and

wherein the quaternary alkyl contains a quaternary carbon atom, which may be directly or indirectly bonded to the phenylene, wherein the quaternary carbon atom is an element having atomic number 6 in the Periodic Table of the Elements that is bonded to four other carbon atoms.

2. The method of claim 1 wherein the first trim catalyst comprises a solution of the first alkane-soluble non-metallocene catalyst dissolved in an alkane solvent and step (B) comprises feeding the solution into the reactor, the solution being free of a support material.

3. The method of claim 1 or 2 further comprising steps (a) and (b): (a) contacting, separately from step (A), a first metallocene precatalyst with an activator and, optionally, a support material so as to make a first metallocene catalyst, optionally free of the support material or disposed on and/or in the support material; and (b) feeding, separately from step (B), the first metallocene catalyst, into the polymerization reactor; and wherein step (C) further comprises polymerizing the olefin monomer with the first metallocene catalyst in the polymerization reactor; thereby making a first bimodal polyolefin composition comprising the first polyolefin polymer and a second polyolefin polymer.

4. The method of claim 3 wherein step (B) comprises feeding the first trim catalyst as a solution of the first alkane-soluble non-metallocene catalyst dissolved in a first alkane solvent into the polymerization reactor; and wherein the step (b) comprises separately feeding a solution of the first metallocene catalyst dissolved in a second alkane solvent into the polymerization reactor; wherein the first and second alkane solvents are the same or different; and wherein the solutions are free of a support material.

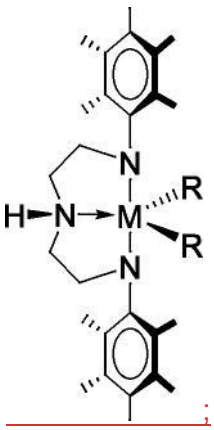
5. The method of claim 3 or 4 further comprising, after the step (C), (D) transitioning the method from the steps (a) and (b) to steps (a1) and (b1), respectively: (a1) contacting a second metallocene precatalyst, which is different than the first metallocene precatalyst in structure of at least one cyclopentadienyl ligand, with an activator, and, optionally, a support material so as to make a second metallocene catalyst, which is different than the first metallocene catalyst, wherein the second metallocene catalyst is free of a support material or is disposed on and/or in the support material; and (b1) decreasing the feeding of the first metallocene catalyst from a steady-state value until the first metallocene catalyst is no longer being fed into the polymerization reactor and independently initiating and increasing feeding of the second metallocene catalyst into the polymerization reactor until the second metallocene catalyst is being fed into the polymerization reactor at a steady-state value; and

wherein step (C) further comprises polymerizing the olefin monomer with the second metallocene catalyst in the polymerization reactor; thereby making a second multimodal polyolefin composition comprising the first polyolefin polymer made by the first trim catalyst and a third polyolefin polymer made by the second metallocene catalyst, wherein the third polyolefin polymer is different than each of the first and second polyolefin polymers.

6. The method of claim 1 wherein the first trim catalyst further comprises a support material on which the first alkane-soluble non-metallocene catalyst is disposed.

7. A method of polymerizing an olefin monomer to make a first bimodal polyolefin composition comprising a first higher molecular weight (HMW) polyolefin component and a first lower molecular weight (LMW) polyolefin component, the method comprising steps (1) to (5): (1) contacting a solution of a first alkane-soluble non-metallocene precatalyst dissolved in an alkane solvent with an activator so as to make a first trim catalyst comprising a first alkane-soluble non-metallocene catalyst; (2) contacting a first metallocene precatalyst and an additional amount of the first alkane-soluble non-metallocene precatalyst with an activator and, optionally, a support material so as to make a first bimodal catalyst system comprising a first metallocene catalyst and an additional amount of the first alkane-soluble non-metallocene catalyst, optionally free of the support material or disposed on and/or in the support material; (3) contacting the first bimodal catalyst system with the first trim catalyst to make a first mixed catalyst system comprising a mixture of the first bimodal catalyst system and the first trim catalyst; (4) feeding the first mixed catalyst system into a polymerization reactor; and (5) polymerizing the olefin monomer with the first mixed catalyst system in the polymerization reactor; thereby making the first HMW polyolefin component and the first LMW polyolefin component of the first bimodal polyolefin composition; wherein the first ASNM Precatalyst is characterized by solubility in hexanes containing at least 60 weight percent n-hexane of at least 0.10 weight percent based on total weight of the first ASNM Precatalyst and hexanes, as measured using Solubility Test Method;

wherein the alkane-soluble non-metallocene precatalyst is a compound of formula (1):



(1)

;

wherein M is a Group 4 metal and each R is independently selected from a silicon-free organic solubilizing group;

wherein each R that is independently selected from a silicon-free organic solubilizing group is independently methyl, an unsubstituted (C_2-C_4)alkyl group, an unsubstituted (C_5-C_{12})alkyl group, an unsubstituted or substituted quaternary-arylalkyl group; or both R groups are bonded together to give R′-R′, wherein R′-R′ is an unsubstituted or substituted (aryl)alkylene;

wherein each R group and R′-R′ group is free of a cyclopentadienyl group, a silicon atom, a carbon-carbon double bond, and a carbon-carbon triple bond;

wherein each substituent independently may be selected from unsubstituted (C_1-C_5)alkyl, halogen, -Oalkyl, and -N(alkyl)$_2$;

wherein each quaternary-arylalkyl group sequentially contains a quaternary alkyl, a phenylene, and a (C_1-C_3)alkylene linker, wherein the quaternary alkyl is bonded to the phenylene, which is bonded to the (C_1-C_3)alkylene linker, which is bonded to the metal M;

wherein the (C_1-C_3)alkylene linker and R′-R′ groups are divalent; and

wherein the quaternary alkyl contains a quaternary carbon atom, which may be directly or indirectly bonded to the phenylene, wherein the quaternary carbon atom is an element having atomic number 6 in the Periodic Table of the Elements that is bonded to four other carbon atoms.

8. The method of claim 7 further comprising, after step (5), (6) transitioning the method from steps (2) to (5) to steps (2a) to (5a), respectively: (2a) contacting a second metallocene precatalyst and a second additional amount of the first alkane-soluble non-metallocene precatalyst with an activator and, optionally, a support material so as to make a second bimodal catalyst system comprising the second metallocene catalyst and the second additional amount of the first alkane-soluble non-metallocene catalyst, optionally free of the support material or disposed on and/or in the support material; (3a) contacting the second bimodal catalyst system with the same trim catalyst of step (1) to make a second mixed catalyst system comprising a mixture of the second bimodal catalyst system and the first trim catalyst; (4a) decreasing the feeding of the first mixed catalyst system from a steady-state value until the first mixed catalyst system is no longer being fed into the polymerization reactor and independently initiating and increasing feeding of the second mixed catalyst system into the polymerization reactor until the second mixed catalyst is being fed into the polymerization reactor at a steady-state value; and (5a) polymerizing the olefin monomer with the second mixed catalyst system in the polymerization reactor; thereby making a second bimodal polyolefin composition comprising the first HMW polyolefin component and

a second LMW polyolefin component, which is different than each of the first HMW polyolefin component and the first LMW polyolefin component.

9. The method of any one of claims 1 to 8 wherein the olefin monomer is any one of (i) to (vii): (i) ethylene; (ii) propylene; (iii) a (C_4-C_{20})alpha-olefin; (iv) 1,3-butadiene; (v) a combination of (i) and (ii); (vi) a combination of (i) and (iii); and (vii) a combination of (i), (ii), and (iv); and wherein the first polyolefin polymer or the HMW polyolefin component respectively comprises any one of (a) to (g): (a) a polyethylene homopolymer; (b) a polypropylene homopolymer; (c) a poly(C_4-C_{20})alpha-olefin polymer; (d) a polybutadiene polymer; (e) an ethylene-propylene copolymer; (f) a poly(ethylene-*co*-(C_4-C_{20})alpha-olefin) copolymer; and (g) an ethylene-propylene-butadiene copolymer.

10. The method of any one of claims 1 to 9 wherein the first polyolefin polymer or the HMW polyolefin component has a weight-average molecular weight of at least 110,000 grams per mole (g/mol).

11. The method of any one of claims 1 to 10 wherein the polymerizing is a gas phase polymerizing process and the reactor is a single gas phase polymerization reactor.

12. The method of any one of claims 1 to 11 further comprising transitioning from step (B) to step (B1) feeding to the polymerization reactor a second trim catalyst, which is made by contacting a solution of a second alkane-soluble non-metallocene precatalyst dissolved in an alkane solvent with an activator to make a second alkane-soluble non-metallocene catalyst; wherein the second alkane-soluble non-metallocene precatalyst is different than the first alkane-soluble non-metallocene precatalyst in structure of at least one non-metallocene ligand and the second alkane-soluble non-metallocene catalyst is different than the first alkane-soluble non-metallocene catalyst in structure of the at least one non-metallocene ligand; wherein the second alkane-soluble non-metallocene precatalyst is characterized by solubility in hexanes containing at least 60 weight percent n-hexane of at least 0.10 weight percent based on total weight of the second alkane-soluble non-metallocene precatalyst and hexanes, as measured using Solubility Test Method; and wherein the transitioning comprises decreasing the feeding of the first trim catalyst from a steady-state value until the first trim catalyst is no longer being fed into the polymerization reactor and independently initiating and increasing the feeding of the second trim catalyst into the polymerization reactor until the second trim catalyst is being fed into the polymerization reactor at a steady-state value.

13. The method of any one of claims 1 to 12 wherein the first alkane-soluble non-metallocene precatalyst, and any second alkane-soluble non-metallocene precatalyst, independently is characterized by solubility in hexanes containing at least 60 weight percent n-hexane ($CH_3(CH_2)_4CH_3$) of from 0.50 to 24 wt% based on total weight thereof.