polymerization reaction runs so fast and the resulting exotherm gets so high that the polymer in the fluidized bed softens and agglomerates forming chunks and sheets that clog the reactor.

[0006] Our method to avoid this problem is to form a catalytically-active prepolymer composition in a slurry prepolymerization reaction by prepolymerizing under suitable conditions a small amount (compared to full polymerizations making final polymer products) of one or more olefin monomers with an activated catalyst composition that contains a biphenylphenol catalyst. The catalytically-active prepolymer composition made thereby can be used to catalyze a gas-phase fluidized bed polymerization. The slurry phase prepolymerization for making the catalytically-active prepolymer composition can be performed under suitable conditions that moderate the initial light-off of the catalyst and provide a high level of diluent to moderate the exotherm that occurs at catalyst light-off. The suitable conditions for the prepolymerization reaction are described later and are selected such that the resulting catalytically-active prepolymer composition remains capable of initiating and catalyzing substantial further polymerization of the one or more olefin monomers. The catalytically-active prepolymer composition has a smoother activation when introduced into the gas-phase fluidized bed polymerization.

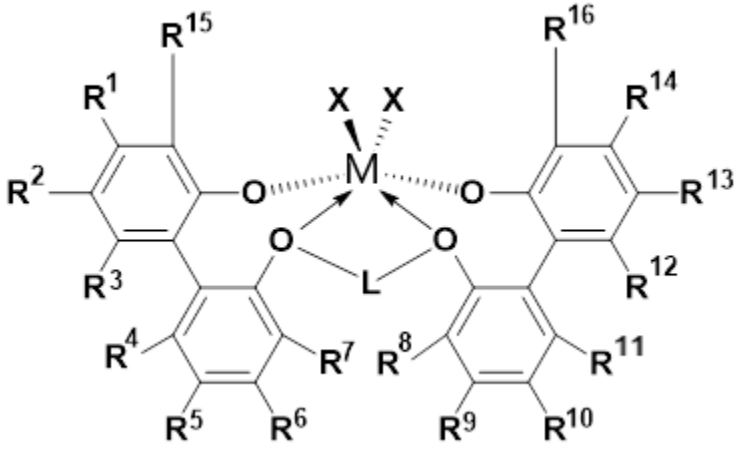
[0007] In this description, “prepolymerization” means a polymerization that makes an intermediate polymer product, which is not the complete intended final polymer product. Likewise, a “prepolymer” is an intermediate polymer product that is not intended to be the final polymer product. “Prepolymerization” reactions in this invention are the same reaction by the same mechanism as an ordinary polymerization and make a similar product, but the reaction conditions may be selected to limit the yield of prepolymer to lower yield than would ordinarily be produced in an ordinary polymerization. In prepolymer compositions, the weight ratio of prepolymer to catalyst remnant is lower than the intended weight ratio of (co)polymer to catalyst remnant in the final intended polymer product. Further, in catalytically-active prepolymer compositions, the prepolymer is mixed with active remnants of the catalyst composition used to make the prepolymer. Prepolymers are not necessarily lower molecular-weight than the intended final polymer product. The prepolymers in the catalytically-active prepolymer composition of the present invention may or may not build further molecular weight when the catalytically-active prepolymer composition is used to catalyze a final polymerization reaction. For clarity, the term “prepolymer” may refer to both a homopolymer and a copolymer.

[0008] The disclosure relates to a process for making a catalytically-active prepolymer composition in a slurry-phase prepolymerization reaction, comprising contacting:

(a) a catalyst composition comprising a biphenylphenol catalyst made by contacting a biphenylphenol procatalyst and an activator; and

(b) one or more olefin monomers,

in a diluent under suitable conditions to prepolymerize the one or more olefin monomers with a yield of 5 parts to 600 parts of catalytically-active prepolymer composition per 1 part of the catalyst composition by weight, wherein the biphenylphenol procatalyst is of Formula I:



I,

wherein each of R^7 and R^8 is independently a C_1 to C_{20} alkyl, aryl or aralkyl, halogen, or a hydrogen;

wherein each of R^4 and R^{11} is independently a hydrogen, alkyl or a halogen;

wherein each of R^5 and R^{10} is independently a C_1 to C_{20} alkyl, aryl, aralkyl, halogen, an alkyl-or aryl-substituted silyl, or a hydrogen;

wherein each of R^2 and R^{13} is independently a C_1 to C_{20} alkyl, aryl or aralkyl or a hydrogen;

wherein each of R^{15} and R^{16} is independently a 2,7-disubstituted carbazol-9-yl;

wherein each of R^1, R^3, R^6, R^9, R^{12}, and R^{14} is independently a hydrogen or alkyl;

wherein L is a saturated C_2-C_3 alkylene that forms a 2-carbon bridge or 3-carbon bridge between the two oxygen atoms to which L is bonded;

wherein each X is independently halogen, a hydrogen, a (C_1-C_{20})alkyl, a (C_7-C_{20})aralkyl, a (C_1-C_6)alkyl-substituted (C_6-C_{12})aryl, or a (C_1-C_6)alkyl-substituted benzyl, $-CH_2Si(R^C)_3$, where R^C is C_1-C_{12} hydrocarbon; and

wherein M is zirconium or hafnium.

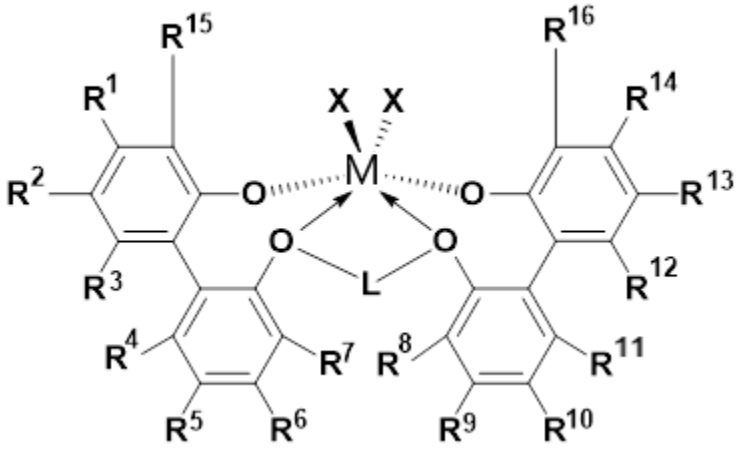
[0008a] A first aspect of the present disclosure is a process for making a catalytically-active prepolymer composition in a slurry-phase prepolymerization reaction, comprising contacting:

(a) a catalyst composition comprising a biphenylphenol catalyst made by activating a biphenylphenol procatalyst with an activator; and

(b) one or more olefin monomers,

in a diluent under suitable conditions to polymerize the one or more olefin monomers with a yield of 5 parts to 600 parts of the catalytically-active prepolymer composition per 1 part of the catalyst composition by weight;

wherein the biphenylphenol procatalyst is of Formula I:



I,

wherein each of R^7 and R^8 is independently a C_1 to C_{20} alkyl, aryl or aralkyl, halogen, or a hydrogen;

wherein each of R^4 and R^{11} is independently a hydrogen, alkyl or a halogen;

wherein each of R^5 and R^{10} is independently a C_1 to C_{20} alkyl, aryl, aralkyl, halogen, an alkyl-or aryl-substituted silyl, or a hydrogen;

wherein each of R^2 and R^{13} is independently a C_1 to C_{20} alkyl, aryl or aralkyl or a hydrogen;

wherein each of R^{15} and R^{16} is independently a 2,7-disubstituted carbazol-9-yl;

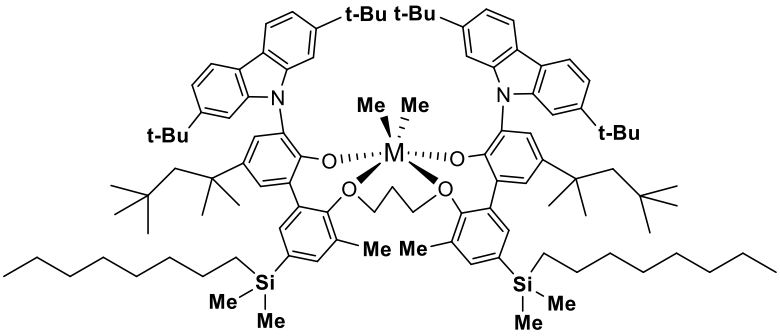
wherein each of R^1, R^3, R^6, R^9, R^{12}, and R^{14} is independently a hydrogen or alkyl;

wherein L is a saturated C_2-C_3 alkylene that forms a 2-carbon bridge or 3-carbon bridge between the two oxygen atoms to which L is bonded;

wherein each X is independently halogen, a hydrogen, a (C_1-C_{20})alkyl, a (C_7-C_{20})aralkyl, a (C_1-C_6)alkyl-substituted (C_6-C_{12})aryl, or a (C_1-C_6)alkyl-substituted benzyl, $-CH_2Si(R^C)_3$, where R^C is C_1-C_{12} hydrocarbon; and

wherein M is zirconium or hafnium;

wherein the biphenylphenol procatalyst meets the following formula:



wherein M is a zirconium ion or a hafnium ion, t-Bu refers to a tertiary butyl group, and Me refers to a methyl group.

[0009] The present disclosure also provides a process to make a polyolefin (co)polymer, comprising the steps of:

(a) making a catalytically-active prepolymer composition in a slurry-phase prepolymerization reaction as previously described or as described in any one of Embodiments 2 to 9 disclosed later; and

(b) using the catalytically-active prepolymer composition to catalyze polymerization of further one or more olefin monomers under conditions to make the polyolefin (co)polymer. (Mole percentages are based on the total quantity of the one or more olefin monomers.) In some examples the further one or more olefin monomers contain from 80 to 100 mole percent ethylene or propylene and 0 to 20 mole percent of an α-olefin comonomer or a butadiene and the polymerization makes a polyethylene (co)polymer or a polypropylene (co)polymer, respectively.

[0009a] A second aspect of the present disclosure is a process to make a polyolefin (co)polymer, comprising the steps of:

(a) making a catalytically-active prepolymer composition in a slurry-phase prepolymerization reaction as described herein; and

(b) using the catalytically-active prepolymer composition to catalyze gas-phase polymerization of further one or more olefin monomers to make the polyolefin (co)polymer.

[0010] A third aspect of the present disclosure is a catalytically-active prepolymer composition made by the process as described herein. In some examples, the catalytically-active prepolymer composition comprises:

(1) an olefin prepolymer component consisting essentially of one or more olefin prepolymers and

(2) a residual catalyst component consisting essentially of remnants of the catalyst composition left over after the prepolymerization reaction; and

wherein: (a) the olefin prepolymer component that has a number average molecular weight (M_n) between 5000 g/mol and 50,000 g/mol; and (b) the weight ratio of the olefin prepolymer component to the residual catalyst component is from 5:1 to 600:1.

[0011] The catalytically-active prepolymer composition can be used to catalyze polymerization of one or more olefin monomers, such as in a gas-phase fluidized bed

polymerization. The resulting polymerization can proceed smoothly to completion without excessive exotherm or the agglomeration that an exotherm can cause.

[0012] Without intending to be bound, we hypothesize that the slurry-phase prepolymerization allows a controlled growth of the prepolymer with better heat transfer. Then, the prepolymer component in the catalytically-active prepolymer composition supplies higher surface area to dissipate the heat and lower activity at initiation in the final polymerization reaction.

CLAIMS

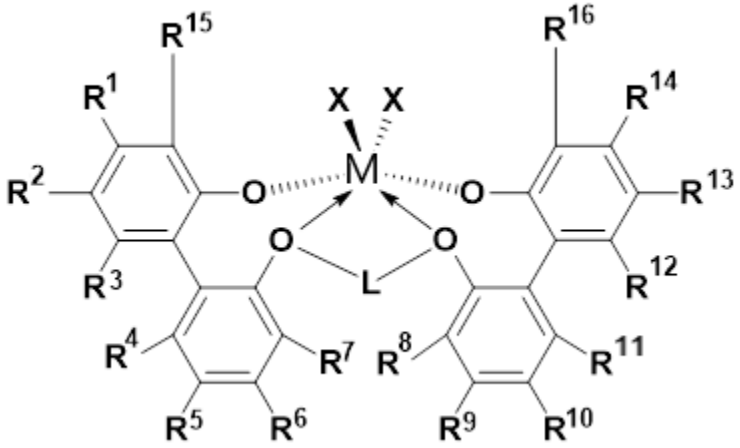
1. A process for making a catalytically-active prepolymer composition in a slurry-phase prepolymerization reaction, comprising contacting:

(a) a catalyst composition comprising a biphenylphenol catalyst made by activating a biphenylphenol procatalyst with an activator; and

(b) one or more olefin monomers,

in a diluent under suitable conditions to polymerize the one or more olefin monomers with a yield of 5 parts to 600 parts of the catalytically-active prepolymer composition per 1 part of the catalyst composition by weight;

wherein the biphenylphenol procatalyst is of Formula I:



I,

wherein each of R^7 and R^8 is independently a C_1 to C_{20} alkyl, aryl or aralkyl, halogen, or a hydrogen;

wherein each of R^4 and R^{11} is independently a hydrogen, alkyl or a halogen;

wherein each of R^5 and R^{10} is independently a C_1 to C_{20} alkyl, aryl, aralkyl, halogen, an alkyl-or aryl-substituted silyl, or a hydrogen;

wherein each of R^2 and R^{13} is independently a C_1 to C_{20} alkyl, aryl or aralkyl or a hydrogen;

wherein each of R^{15} and R^{16} is independently a 2,7-disubstituted carbazol-9-yl;

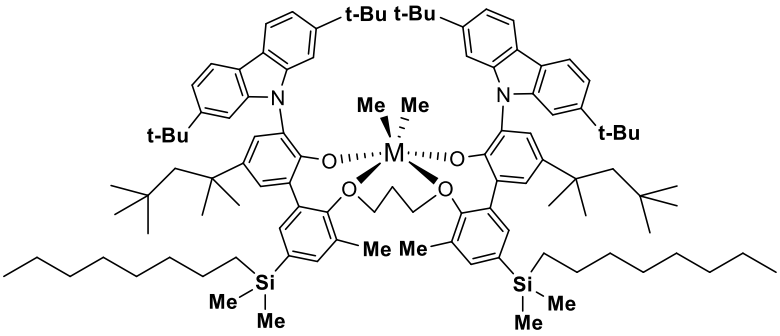
wherein each of R^1, R^3, R^6, R^9, R^{12}, and R^{14} is independently a hydrogen or alkyl;

wherein L is a saturated C_2-C_3 alkylene that forms a 2-carbon bridge or 3-carbon bridge between the two oxygen atoms to which L is bonded;

wherein each X is independently halogen, a hydrogen, a (C_1-C_{20})alkyl, a (C_7-C_{20})aralkyl, a (C_1-C_6)alkyl-substituted (C_6-C_{12})aryl, or a (C_1-C_6)alkyl-substituted benzyl, $-CH_2Si(R^C)_3$, where R^C is C_1-C_{12} hydrocarbon; and

wherein M is zirconium or hafnium;

wherein the biphenylphenol procatalyst meets the following formula:



wherein M is a zirconium ion or a hafnium ion, t-Bu refers to a tertiary butyl group, and Me refers to a methyl group.

2. The process as described in Claim 1 wherein the one or more olefin monomers comprise 80 to 100 mole percent ethylene monomer and 0 to 20 mole percent of an α-olefin comonomer that contains from 4 to 8 carbon atoms, based on total quantity of the one or more olefin monomers.
3. The process as described in any one of Claims 1 to 2 wherein the yield of the catalytically-active prepolymer composition is 5 parts to 400 parts of the catalytically-active prepolymer composition per 1 part of the catalyst composition by weight.
4. The process as described in any one of Claims 1 to 3 wherein the yield of the catalytically-active prepolymer composition is 5 parts to 200 parts of catalytically-active prepolymer composition per 1 part of the catalyst composition by weight.
5. The process as described in any one of Claims 1 to 4 wherein the diluent is an alkane that contains from 4 to 10 carbon atoms.
6. The process as described in any one of Claims 1 to 5 wherein the weight ratio of the diluent to total olefin monomers is from 5:1 to 800:1.
7. The process as described in any one of Claims 1 to 6 wherein the suitable conditions comprise a temperature of the slurry-phase prepolymerization reaction from 25°C to 80°C.

8 The process as described in any one of claims 1 to 7, wherein the yield of 5 parts to 600 parts of the catalytically-active prepolymer composition per 1 part of the catalyst composition by weight is achieved by controlling the total amount of the one or more olefin monomers used in the contacting step.

9. A process to make a polyolefin (co)polymer, comprising the steps of:
   (a) making a catalytically-active prepolymer composition in a slurry-phase prepolymerization reaction as described in any one of Claims 1 to 8; and
   (b) using the catalytically-active prepolymer composition to catalyze gas-phase polymerization of further one or more olefin monomers to make the polyolefin (co)polymer.
10. The process as described in Claim 9 wherein the temperature of the slurry-phase prepolymerization reaction is at least 5°C lower than the temperature of the gas phase polymerization.
11. The process as described in any one of Claims 9 and 10 wherein the gas phase polymerization step takes place in the presence of a diluent that is the same as the diluent used in the slurry-phase prepolymerization reaction.
12. The process as described in any one of Claims 9 to 11 (i) wherein the catalytically-active prepolymer composition is fed directly from the slurry-phase prepolymerization step to the fluidized bed polymerization step without recovering and passivating the catalytically-active prepolymer composition; or (ii) wherein the catalytically-active prepolymer composition is recovered after the slurry-phase prepolymerization step, passivated, and stored before being used in the gas-phase polymerization step; or both (i) and (ii).
13. The process as described in any one of Claims 9 to 12 which comprises the following steps:
   (a) making the catalyst composition by depositing the biphenylphenol procatalyst and the activator on a silicon-containing carrier material, wherein the activator contains aluminum and contacts the biphenylphenol procatalyst;
   (b) performing the slurry-phase prepolymerization reaction by contacting the catalyst composition with one or more olefin monomers that contain 80 to 100 mole percent ethylene and 0 to 20 mole percent of an α-olefin comonomer having 4 to 8 carbons in an alkane diluent having 3 to 12 carbon atoms, to form a catalytically-active prepolymer composition that contains both an olefin prepolymer component and a residual catalyst component in a weight ratio from 5:1 and 600:1, wherein the olefin prepolymer component consists essentially of one or more olefin prepolymers and wherein the residual catalyst component consists essentially of remnants of the catalyst composition; and

(c) performing a gas-phase fluidized bed polymerization reaction by contacting the catalytically-active prepolymer composition with further one or more olefin monomers that contain 80 to 100 mole percent ethylene and 0 to 20 mole percent of an α-olefin comonomer having 4 to 8 carbons under conditions suitable to make a polyolefin (co)polymer.

14. A catalytically-active prepolymer composition made by the process as described in any one of Claims 1 to 8.