

CAPPED DUAL-HEADED ORGANOALUMINUM COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to, and the benefit of, U.S. provisional application no. 62/611,656, which was filed on December 29, 2017, and is incorporated herein in its entirety.

FIELD

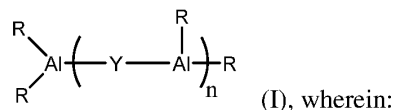
[0001] Embodiments relate to capped dual-headed organoaluminum compositions and processes to prepare the same. Such compositions may be capable of chain shuttling and/or chain transfer. In at least one aspect, the capped dual-headed organoaluminum compositions can be used in olefin polymerization.

BACKGROUND

[0002] In recent years, advances in polymer design have been seen with the use of compositions capable of chain shuttling and/or chain transfer. For example, chain shuttling agents having reversible chain transfer ability with transition metal catalysts have enabled the production of novel olefin block copolymers (OBCs). Currently, the best known compositions capable of chain shuttling and/or chain transfer are simple metal alkyls that typically contain only a single point of attachment to the metal for each polymer chain, such as diethyl zinc which produces polymer chains terminated with zinc metal at one end. More sophisticated compositions capable of chain shuttling and/or chain transfer, such as dual-headed chain shuttling agents, with the alkane moiety attached to two metals, are also known. Indeed, dual-headed compositions capable of chain shuttling and/or chain transfer are of great interest since they can enable the production of new polyolefins, such as telechelic functional polymers, triblock copolymers, etc. However, significant challenges exist for using such dual-headed compositions to produce highly pure telechelic polymer chains in reactors.

SUMMARY

[0003] In certain embodiments, this disclosure relates to a capped dual-headed organoaluminum composition of formula (I):



n is a number from 1 to 100;

Y is a linking group composed of a linear, branched, or cyclic C₄ to C₁₀₀ hydrocarbylene group that optionally includes at least one heteroatom and that is aliphatic or aromatic, wherein Y comprises two points of attachment to Al atoms and at least one of the two points of attachments is -CH₂-;

each R group is independently a substituted or unsubstituted aryl group or a substituted or unsubstituted cyclic alkyl group containing, optionally, at least one heteroatom; and

two R groups attached to the same Al atom can be optionally covalently linked together.

[0004] In further embodiments, this disclosure relates to a process for preparing a capped dual-headed organoaluminum composition of formula (I), the process comprising: (a) combining an aluminum compound, a linking agent, a capping agent, and an optional solvent, and (b) obtaining the capped dual-headed organoaluminum composition of formula (I), wherein:

the aluminum compound has the formula Al(J)₃, wherein each J group is independently hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl or heteroaryl group, wherein at least one J group is hydrogen or an acyclic alkyl group, and, optionally, two J groups can be covalently linked together;

the linking agent is a C₄ to C₁₀₀ hydrocarbon comprising either at least two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom; and

the capping agent is a substituted or unsubstituted cyclic olefin.

[0005] In further embodiments, this disclosure relates to a capped dual-headed organoaluminum composition of formula (I) comprising the reaction product of an aluminum compound, a linking agent, a capping agent, and an optional solvent, wherein:

the aluminum compound has the formula Al(J)₃, wherein each J group is independently hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl or heteroaryl group, wherein at least one J group is a hydrogen or an acyclic alkyl group, and, optionally, two J groups can be covalently linked together;

the linking agent is a C₄ to C₁₀₀ hydrocarbon comprising either at least two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom; and

the capping agent is a substituted or unsubstituted cyclic olefin.

BRIEF DESCRIPTION OF DRAWINGS

[0006] FIG. 1 is the ¹H NMR spectra for Example 1.

[0007] FIG. 2 is the GC/MS spectrum for Example 1.

[0008] FIGS. 3A and 3B are the ¹H NMR spectra for Example 2.

[0009] FIG. 4 is the GC/MS spectrum for Example 2.

[0010] FIG. 5 is the GC/MS spectrum for Example 3.

[0011] FIGS. 6A, 6B, and 6C are the ¹H NMR spectra for Example 4.

[0012] FIG. 7 is the ¹³C NMR spectrum of polyethylene synthesized in the presence of the capped dual-headed organoaluminum composition of Example 3.

[0013] FIG. 8 is the GPC chromatogram of polyethylene synthesized in the presence of the capped dual-headed organoaluminum composition of Example 3.

DEFINITIONS

[0014] All references to the Periodic Table of the Elements 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 percentages are based on weight and all test methods are current as of the filing date of this disclosure. For purposes of United States patent practice, the contents of any referenced patent, patent application or publication are incorporated by reference in their entirety (or its equivalent U.S. version is so incorporated by reference in its entirety), especially with respect to the disclosure of synthetic techniques, product and processing designs, polymers, catalysts, definitions (to the extent not inconsistent with any definitions specifically provided in this disclosure), and general knowledge in the art.

[0015] Number ranges in this disclosure are approximate and, thus, may include values outside of the ranges unless otherwise indicated. The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges

containing explicit values (e.g., 1, or 2, or 3 to 5, or 6, or 7), any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.). The numerical ranges disclosed herein further include the fractions between any two explicit values

[0016] In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control.

[0017] The terms “chain shuttling agent” and “chain transfer agent” refer to those known to one of ordinary skill in the art. Specifically, the term “shuttling agent” or “chain shuttling agent” refers to a compound or mixture of compounds that is capable of causing polymeryl transfer between various active catalyst sites under conditions of polymerization. That is, transfer of a polymer fragment occurs both to and from an active catalyst site in a facile and reversible manner. In contrast to a shuttling agent or chain shuttling agent, an agent that acts merely as a “chain transfer agent,” such as some main-group alkyl compounds, may exchange, for example, an alkyl group on the chain transfer agent with the growing polymer chain on the catalyst, which generally results in termination of the polymer chain growth. In this event, the main-group center may act as a repository for a dead polymer chain, rather than engaging in reversible transfer with a catalyst site in the manner in which a chain shuttling agent does.

Desirably, the intermediate formed between the chain shuttling agent and the polymeryl chain is not sufficiently stable relative to exchange between this intermediate and any other growing polymeryl chain, such that chain termination is relatively rare.

[0018] The term “derivative” used herein refers to the reaction product of a chemical species after the insertion reaction of said chemical species into metal alkyl or metal hydride bonds. For example, and without limitation, the “Y^C” in (R)₂—Al[—Y^C—Al(R)]_n—R can define the derivative of the linking agent CH₂=CH(CH₂)₆CH=CH₂ when said linking agent is reacted with Al(iBu)₃ to form (iBu)₂—Al[—CH₂(CH₂)₈CH₂—Al(iBu)]_n—iBu. In this non-limiting example, Y^C is —CH₂(CH₂)₈CH₂—, a linking group which is the derivative of the linking agent CH₂=CH(CH₂)₆CH=CH₂ after insertion of said linking agent into Al-H bonds.

[0019] The term “linking agent” is a chemical species whose derivative links multiple metal species together in a molecule by inserting into a metal alkyl or metal hydride bond of each metal. In the above non-limiting example, CH₂=CH(CH₂)₆CH=CH is a

linking agent which joins $n+1$ aluminum species to form the species $(iBu)_2-Al[-CH_2(CH_2)_8CH_2-Al(iBu)]_n-iBu$. After insertion, the linking agent becomes the linking group $-CH_2(CH_2)_8CH_2-$.

[0020] The terms “capped” or “capping group” refer to the derivative of a “capping agent,” where the capping agent forms a more sterically hindered metal alkyl/aryl bond such that the rate of further chain transfer or chain shuttling reactions from this derivative is very low. For example, and without limitation, the R groups of the composition of formula (I) are capping groups which are derivatives of capping agents, where the capping agents are substituted or unsubstituted cyclic olefins, optionally containing at least one heteroatom.

[0021] With reference to the composition of formula (I) or any structural formulae falling within formula (I), the symbol * used herein refers to a carbon-metal bond serving as the point of attachment between the carbon of a substituent group and the aluminum metal of the composition of formula (I).

[0022] “Co-catalysts” refers to compounds that can activate a procatalyst to form an active catalyst composition/system capable of polymerization of unsaturated monomers. “Co-catalyst” is used interchangeably with “activator” and like terms.

[0023] “Procatalyst” refers to a transition metal compound that, when combined with an activator, is capable of polymerization of unsaturated monomers. Suitable procatalysts for the present disclosure include those that either require or do not require a co-catalyst to become an active catalyst capable of polymerizing unsaturated monomers. “Procatalyst” is used interchangeably with “catalyst precursor,” “transition metal catalyst,” “transition metal catalyst precursor,” “metal complex,” and like terms. Suitable procatalysts include those known in the art, such as those disclosed in WO 2005/090426, WO 2005/090427, WO 2007/035485, WO 2009/012215, WO 2014/105411, U.S. Patent Publication Nos. 2006/0199930, 2007/0167578, 2008/0311812, and U.S. Patent Nos. 7,355,089 B2, 8,058,373 B2, and 8,785,554 B2, all of which are incorporated herein by reference in their entirety.

[0024] “Catalyst system” refers to a procatalyst or the combination of a procatalyst and an activator, with or without a support, capable of olefin polymerization. “Catalyst system” is used interchangeably with “active catalyst,” “active catalyst composition,” “olefin polymerization catalyst,” and like terms.

[0025] "Polymer" refers to a compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, and the term interpolymer as defined below. It also embraces all forms of interpolymers, e.g., random, block, homogeneous, heterogeneous, etc.

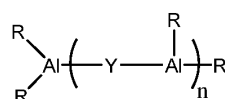
[0026] "Interpolymer" and "copolymer" refer to a polymer prepared by the polymerization of at least two different types of monomers. These generic terms include both classical copolymers, i.e., polymers prepared from two different types of monomers, and polymers prepared from more than two different types of monomers, e.g., terpolymers, tetrapolymers, etc.

[0027] The term "block copolymer" or "segmented copolymer" refers to a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined (covalently bonded) end-to-end with respect to polymerized functionality, rather than in pendent or grafted fashion. The blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the type of crystallinity (e.g., polyethylene versus polypropylene), the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, and/or any other chemical or physical property. The block copolymers are characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn) and block length distribution, e.g., based on the effect of the use of a shuttling agent(s) in combination with catalyst systems.

DETAILED DESCRIPTION

[0028] All schemes and discussions below are by way of example only and are not meant to be limiting in any way. As noted herein, dual-headed compositions are of great interest since they can enable production of telechelic functional polymers. For example, and without limitation, reference is made to non-limiting Structure 1. Structure 1 represents an exemplary dual-headed composition with a Y linking group sandwiched between two aluminum atoms. Y may be, for example, a linear, branched, or cyclic C₄ to C₁₀₀ hydrocarbylene group that optionally includes at least one

heteroatom (B, O, S, N, F, Cl or Si) and that is aliphatic or aromatic. The Y linking group links two separate Al atoms and is attached to each Al atom via points of attachment. The points of attachment are groups within (i.e., fragments of) the Y linking group, and at least one point of attachment is an ethylene group, $-\text{CH}_2-$. Each of the terminal R groups may be a substituted or unsubstituted aryl group or a substituted or unsubstituted cyclic alkyl group and may, optionally, include at least one heteroatom. Two R groups attached to the same Al atom can be optionally covalently linked together. The Y linking group can then, during olefin polymerization, grow into a polymer chain with both terminal ends of the chain bonded to the aluminum atoms via terminal polymeryl-metal bonds. Subsequently, the terminal polymeryl-metal bonds may be transformed to desired functional groups via functionalization chemistry, thereby resulting in a desired di-functional (telechelic) polymer chain. The composition of non-limiting Structure 1 may be in monomeric ($n=1$) or oligomeric ($n>1$) forms.



Structure 1.

[0029] Structure 1 contains capping groups (R) that have very low rates of chain transfer or chain shuttling with a catalyst and will, therefore, not grow into polymer chains (i.e., no unwanted mono-functional chains are produced). Specifically, as seen in the composition of formula (I), the terminal R groups (capping groups) may form sterically hindered metal-carbon bonds such that chain transfer or chain shuttling on these sterically hindered sites are kinetically disfavored in competition with the less hindered bonds between the metal atoms and the Y linking group (i.e., the derivative of a linking agent). Accordingly, unwanted mono-functional polymer chains are prevented from growing, as the capping groups make the chain transfer or chain shuttling reaction and polymer growth occur selectively on the less-hindered, Y linking group of the composition of formula (I). As a result, only desired di-functional polymer chains will grow from the Y linking group via olefin polymerization and functionalization, thereby enabling pure telechelic polymers.

[0030] If the R groups of Structure 1 were simple alkyl groups rather than capping groups, they could lead to monofunctional polymer chains by chain transfer polymerization. A way to reduce the amount of unwanted mono-functional polymer chains relative to the desired di-functional polymer chains (grown from the Y linking group) is to increase the (n) value of the composition; however, such an approach would result in higher in-reactor molecular weight chains which would cause reactor operability issues (e.g., high viscosity), especially for solution processes. Accordingly, the use of capping groups (R) is important as this allows for the formation of highly pure difunctional polymers exclusively from the Y linking group.

Process for Preparing Capped Dual-headed Organoaluminum Compositions

[0031] The composition of formula (I) can be prepared from the reaction resulting from combining an aluminum compound, a linking agent, and a capping agent. In certain embodiments, the capping group can be part of the aluminum compound; thus the composition of formula (I) can be prepared from the reaction resulting from combining an aluminum compound and a linking agent. In this case, the R groups of formula (I) will be J groups instead. These reactions can occur in the absence of (neat) or in the presence of solvent(s). Suitable solvents include but are not limited to non-polar solvents, such as xylenes, toluene, hexane, pentane, benzene, or combinations thereof.

[0032] Accordingly, the composition of formula (I) can be prepared by a process comprising: (a) combining an aluminum compound, a linking agent, a capping agent, and an optional solvent (or, in certain embodiments, combining an aluminum compound, a linking agent, and an optional solvent), and (b) obtaining the composition of formula (I), wherein: the aluminum compound has the formula $Al(J)_3$, where each J group is independently hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl or heteroaryl group, wherein at least one J group is hydrogen or an acyclic alkyl group, and, optionally, two J groups can be covalently linked together; the linking agent is a C_4 to C_{100} hydrocarbon comprising either at least two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom; and the capping agent is a substituted or unsubstituted cyclic olefin.

[0033] The reaction resulting from combining an aluminum compound, a linking agent, a capping agent, and an optional solvent (or, in certain embodiments, combining an

aluminum compound, a linking agent, and an optional solvent) may be conducted at a temperature of from 50 °C to 200 °C, or from 80 °C to 180 °C, or from 100 °C to 150 °C. These elevated temperatures facilitate the removal of the J groups (e.g., alkyl groups) of the aluminum compound via beta-hydride elimination resulting in insertion of the linking agent and the capping agent into the resulting Al-H bonds to form the composition of formula (I).

[0034] Accordingly, in certain embodiments, the composition of formula (I) can be prepared by a process comprising: (a) combining an aluminum compound, a linking agent, a capping agent, and an optional solvent (or, in certain embodiments, combining an aluminum compound, a linking agent, and an optional solvent) at a temperature of from 50 °C to 200 °C (or from 80 °C to 180 °C or from 100 °C to 150 °C), and (b) obtaining the composition of formula (I), wherein: the aluminum compound has the formula $Al(J)_3$, where each J group is independently hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl or heteroaryl group, wherein at least one J group is hydrogen or an acyclic alkyl group, and, optionally, two J groups can be covalently linked together; the linking agent is a C_4 to C_{100} hydrocarbon comprising either at least two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom; and the capping agent is a substituted or unsubstituted cyclic olefin.

[0035] The reaction resulting from combining an aluminum compound, a linking agent, a capping agent, and an optional solvent (or, in certain embodiments, combining an aluminum compound, a linking agent, and an optional solvent) may require a reaction period of from 30 minutes to 200 hours depending on the temperature at which the reaction is conducted. For example, and without limitation, a reaction period of 1 to 2 hours may be needed if the reaction is conducted at 150 °C, a reaction period of 2 to 5 hours may be needed if the reaction is conducted at 120 °C, and a reaction period of 20 to 200 hours may be needed if the reaction is conducted at 60 °C.

[0036] Accordingly, in certain embodiments, the composition of formula (I) can be prepared by a process comprising: (a) combining an aluminum compound, a linking agent, and an optional solvent (or, in certain embodiments, combining an aluminum compound, a linking agent, and an optional solvent) at a temperature of from 50 °C to 200 °C (or from 80 °C to 180 °C or from 100 °C to 150 °C) for a period of from 30

minutes to 200 hours (or from 30 minutes to 100 hours, or from 1 hour to 50 hours, or from 1 hour to 30 hours, or from 1 hour to 25 hours, or from 1 hour to 15 hours, or from 1 hour to 10 hours, or from 1 hour to 5 hours), and (b) obtaining the composition of formula (I), wherein: the aluminum compound has the formula $\text{Al}(\text{J})_3$, where each J group is independently hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl or heteroaryl group, wherein at least one J group is hydrogen or an acyclic alkyl group, and, optionally, two J groups can be covalently linked together; the linking agent is a C_4 to C_{100} hydrocarbon comprising either at least two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom; and the capping agent is a substituted or unsubstituted cyclic olefin.

[0037] In certain embodiments of the process for preparing the composition of formula (I), the linking agent:aluminum compound:capping agent ratio is $n:(n+1):(n+3)$, where n can be a number from 1 to 10. In certain embodiments of the process for preparing the composition of formula (I), the linking agent:aluminum compound ratio is $n:(n+1)$, where n can be a number from 1 to 10.

[0038] In the process for preparing the composition of formula (I), the aluminum compound, the linking agent, the capping agent, and the optional solvent may be combined in any order. In certain embodiments, the aluminum compound, the linking agent, the capping agent, and the optional solvent may be combined in one step. In further embodiments, the aluminum compound, the linking agent, the capping agent, and the optional solvent may be combined in more than one step. For example, the aluminum compound, the capping agent, and the optional solvent may be combined first followed by subsequent addition of the linking agent; or, the aluminum compound, the linking agent, and the optional solvent may be combined first followed by subsequent addition of the capping agent; or in certain embodiments where the capping agent is part of the aluminum compound, the aluminum compound, the linking agent, and the optional solvent may be combined at the same time.

Aluminum compound

[0039] Aluminum compounds are defined herein as compounds with the formula $\text{Al}(\text{J})_3$, where each J group independently is hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl or heteroaryl group, wherein at least

one J group is hydrogen or an acyclic alkyl group, and, optionally, two J groups can be covalently linked together. Optionally, one J group, or each of two or three J groups, can be a hydrogen atom. In certain embodiments, one J group, or each of two or three J groups, is an acyclic alkyl group containing 1 to 30 carbon atoms or 2 to 20 carbon atoms. In certain embodiments, one J group, or each of two or three J groups, is not hydrogen. In further embodiments, one J group, or each of two or three J groups, is not methyl. In further embodiments, one J group, or each of two or three J groups, is a C₁ to C₃₀ acyclic alkyl group or a C₂ to C₂₀ acyclic alkyl group. In certain embodiments, one J group, or each of two or three J groups, is a branched C₃ to C₃₀ acyclic alkyl group.

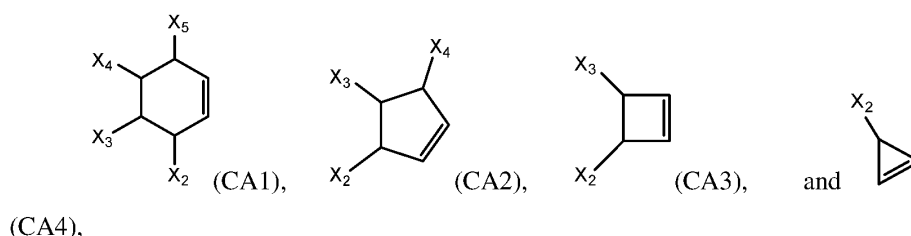
[0040] Suitable J groups include but are not limited to methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, aryl, and all isomers thereof. Trialkylaluminum compounds and dialkylaluminum-hydride compounds are suitable reagents. Useful trialkylaluminum compounds include but are not limited to trimethyl aluminum, triethyl aluminum, triisobutyl aluminum, tripropyl aluminum, tributyl aluminum, trihexyl aluminum, triisohexyl aluminum, trioctyl aluminum, triisooctyl aluminum, tripentyl aluminum, tridecyl aluminum, tribranched alkyl aluminums, tricycloalkyl aluminums, triphenyl aluminum, tritolyl aluminum, and the like. Useful dialkylaluminum compounds include but are not limited to dimethylaluminum-hydride, diethylaluminum-hydride, diisobutylaluminum-hydride, dibutylaluminum-hydride, dipropylaluminum-hydride, dihexylaluminum-hydride, diisohexylaluminum-hydride, dioctylaluminum-hydride, diisooctylaluminum-hydride, dipentylaluminum-hydride, didecylaluminum-hydride, dicycloalkyl aluminums, diphenylaluminum-hydride, ditolylaluminum-hydride, and the like.

Capping Groups

[0041] The terminal R groups of the composition of formula (I) are capping groups, which are derivatives of capping agents. In certain embodiments, the capping agents of this disclosure are substituted or unsubstituted cyclic olefins or substituted or unsubstituted aryl group which, optionally, may contain at least one heteroatom. The cyclic olefins may be monocyclic or polycyclic. Suitable cyclic olefins include but are not limited to 5-ethylidene-2-norbornene (ENB), cyclohexene, norbornene, vinyl norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene,

cyclooctene, cyclooctadiene, cyclododecene, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, benzonorbornadiene, 7-oxanorbornene, 7-oxanorbornadiene, and substituted derivatives thereof.

[0042] In certain embodiments, the terminal R groups (i.e., capping groups) of the composition of formula (I) are derivatives of cyclic olefins, which are alkenes that form sterically hindered metal-carbon bonds. In further embodiments, the terminal R groups (i.e., capping groups) of the composition of formula (I) are derivatives of cyclic olefins, wherein the cyclic olefins (i.e., capping agents) are selected from the group consisting of the following structures CA1 to CA4:



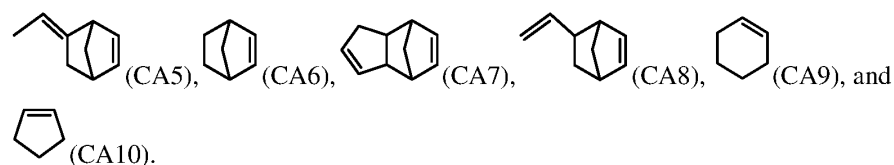
wherein:

each X₂, X₃, X₄, and X₅ is independently hydrogen, a substituted or unsubstituted C₁ to C₂₀ alkyl, alkylene or alkylidene group, or a substituted or unsubstituted C₆ to C₂₀ aryl group;

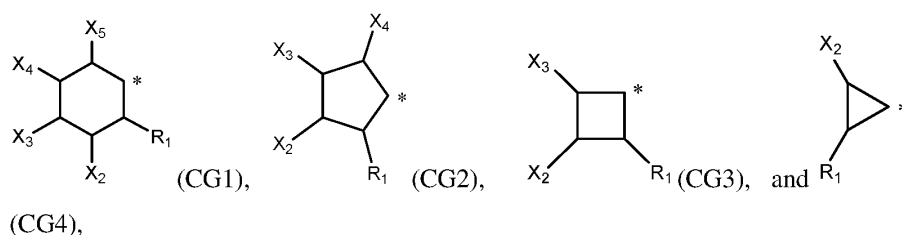
each X₂, X₃, X₄, and X₅ optionally includes at least one heteroatom; and

in each of structures CA1 to CA3, two of the groups selected from X₂, X₃, X₄, and X₅ may optionally join to form cyclic structures.

[0043] In certain embodiments, the terminal R groups (i.e., capping groups) of the composition of formula (I) are selected from derivatives of cyclic olefins, wherein the cyclic olefins (i.e., capping agents) are selected from the group consisting of the following structures CA5 to CA10:



[0044] Accordingly, in certain embodiments, the composition of formula (I) comprises terminal R groups (i.e., capping groups) that are selected from the group consisting of the following structures CG1 to CG4:



wherein:

R_1 is hydrogen or a C_1 to C_{20} alkyl group;

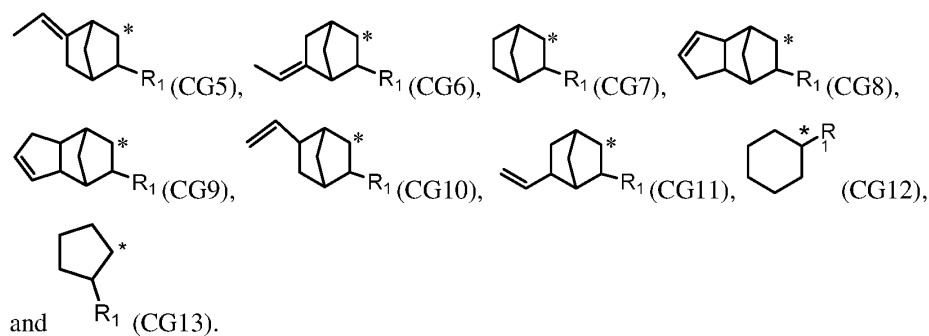
each X_2 , X_3 , X_4 , and X_5 is independently hydrogen, a substituted or unsubstituted C_1 to C_{20} alkyl, alkylene or alkylidene group, or a substituted or unsubstituted C_6 to C_{20} aryl group;

each X_2 , X_3 , X_4 , and X_5 optionally includes at least one heteroatom; and

in each of structures CG1 to CG3, two of the groups selected from X_2 , X_3 , X_4 , and X_5 may optionally join to form cyclic structures.

[0045] With reference to the above definitions, the symbol * refers to a carbon-metal bond serving as the point of attachment between the carbon of a capping group and the aluminum metal of the composition of formula (I).

[0046] In further embodiments, the composition of formula (I) comprises terminal R groups (i.e., capping groups) that are selected from the group consisting of the following structures CG5 to CG13:



wherein R_1 is hydrogen or a C_1 to C_{20} alkyl group.

[0047] In certain embodiments, R_1 of the terminal R groups (i.e., capping groups) of the composition of formula (I) may be methyl, ethyl, n-propyl, n-butyl, isobutyl, n-hexyl, isohexyl, n-octyl, or isooctyl.

Linking Group

[0048] In the composition of formula (I), Y is a linking group, which is a linear, branched, or cyclic C₄ to C₁₀₀ hydrocarbylene group that optionally includes at least one heteroatom and that is aliphatic or aromatic. Linking group Y is the derivative of a linking agent, wherein the linking agent is a C₄ to C₁₀₀ hydrocarbon comprising either at least two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom. Suitable linking agents must be able to insert into aluminum-hydride bonds such that derivatives of the linking agents are sandwiched between two aluminum atoms. As discussed above, Y of the composition of formula (I) is a linking group that can transfer to an active catalyst and grow during olefin polymerization into a polymer chain as a result of chain transfer/chain shuttling between the active catalyst and the aluminum species to form a precursor for a telechelic polymer. Subsequent functionalization will then result in formation of the telechelic polymer.

[0049] In certain embodiments, Y is the derivative of a diene. In other words, the linking agent is a diene. As used herein, the term diene refers to any compound that contains either two vinyl groups or a vinyl group and a cyclic olefin group and, optionally, includes at least one heteroatom. Examples of suitable dienes include hydrocarbon-based dienes, heteroatom-containing hydrocarbon-based dienes such as 1,3-di(ω -alkenyl)-tetramethyldisiloxanes and di(ω -alkenyl)ethers and dienes containing aromatic fragments, such as divinylbenzene.

[0050] Suitable hydrocarbon-based dienes as referred to herein include but are not limited to dienes having the formula CH₂=CH(CH₂)_mCH=CH₂ or CH₂=CH(Ar)_mCH=CH₂, including cyclic and bicyclic analogs thereof, where m is an integer from 0 to 20, and Ar is an aryl group. Examples of these hydrocarbon-based dienes include but are not limited to 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and the like, typically containing from 5 to 40 carbon atoms.

[0051] Heteroatom-containing hydrocarbon-based dienes as referred to herein include dienes which contain at least one B, O, S, N, F, Cl or Si atom, or a combination of atoms. Specific examples of heteroatom-containing hydrocarbon-based dienes include but are not limited to compounds having the formulas O[(CH₂)_mCH=CH₂]₂,

$S[(CH_2)_mCH=CH_2]_2$, $R^A N[(CH_2)_mCH=CH_2]_2$, $(R^B)_2Si[(CH_2)_mCH=CH_2]_2$,
 $Ar[Si(R^B)_2(CH_2)_mCH=CH_2]_2$, $(CH_2)_m[Si(R^B)_2(CH_2)_mCH=CH_2]_2$,
 $(R^B)_3SiOSiR^B[(CH_2)_mCH=CH_2]_2$, and $[Si(R^B)_2(CH_2)_mCH=CH_2]_2O$; wherein m in each
 occurrence is independently an integer from 0 to 20, inclusive, preferably 1 to 20
 inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; R^B in
 each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms,
 inclusive; and Ar is an aryl group.

[0052] Examples of heteroatom-containing hydrocarbon-based dienes include but are
 not limited to divinyl diphenylsilane, 1,4-bis(dimethyl(vinyl)silyl)benzene, 1,5-
 bis(dimethyl(vinyl)silyl)pentane, divinyl ether, di(2-propenyl)ether, di(3-butenyl)ether,
 di(4-pentenyl)ether, di(5-hexenyl)ether, divinyl amine, di(2-propenyl)amine, di(3-
 butenyl)amine, di(4-pentenyl)amine, di(5-hexenyl)amine, divinyl methylamine, di(2-
 propenyl)methylamine, di(3-butenyl)methylamine, di(4-pentenyl)methylamine, di(5-
 hexenyl)methylamine, divinyl thioether, di(2-propenyl)thioether, di(3-
 butenyl)thioether, di(4-pentenyl)thioether, di(5-hexenyl)thioether, divinyl
 dimethylsilane, di(2-propenyl)dimethylsilane, di(3-butenyl)dimethylsilane, di(4-
 pentenyl)dimethylsilane, di(5-hexenyl)dimethylsilane, and the like, typically
 containing from 4 to 40 carbon atoms.

[0053] Further examples of suitable heteroatom containing hydrocarbon-based dienes
 include but are not limited to the disiloxane compounds, such as the 1,1- and the 1,3-
 isomers of divinyl tetramethyldisiloxane (also referred to here as di(ethan-1,2-diyl)
 tetramethyldisiloxane), di(2-propenyl)tetramethyldisiloxane, di(3-
 butenyl)tetramethyldisiloxane, di(4-pentenyl)tetramethyldisiloxane, di(5-
 hexenyl)tetramethyldisiloxane, di(6-heptenyl)tetramethyldisiloxane, di(7-
 octenyl)tetramethyldisiloxane, di(8-nonenyl)tetramethyldisiloxane, di(9-decenyl)-
 tetramethyldisiloxane, divinyltetraethyldisiloxane, di(2-propenyl)tetraethyldisiloxane,
 di(3-butenyl)tetraethyldisiloxane, di(4-pentenyl)tetraethyldisiloxane, di(5-hexenyl)-
 tetraethyldisiloxane, di(6-heptenyl)tetraethyldisiloxane, di(7-
 octenyl)tetraethyldisiloxane, di(8-nonenyl)tetraethyldisiloxane, di(9-
 decenyl)tetraethyldisiloxane, and the like;

[0054] diene compounds containing one cyclic olefin or cyclic alkane such as vinyl
 norbornene, 1,3-divinylcyclopentane, and vinylcyclohexene;

[0055] halogen-containing diene compounds such as 3-chloro-1,4-pentadiene, 3-bromo-3-methyl-1,4-pentadiene, 3-chloro-1,4-hexadiene, 3-chloro-3-methyl-1,4-hexadiene, 3-bromo-4-methyl-1,4-hexadiene, 3-chloro-5-methyl-1,4-hexadiene, 3-bromo-4,5-dimethyl-1,4-hexadiene, 3-bromo-1,5-hexadiene, 3-chloro-3-methyl-1,5-hexadiene, 3-bromo-1,5-heptadiene, 3-chloro-3-methyl-1,5-heptadiene, 4-bromo-1,6-heptadiene, 3-chloro-4-methyl-1,6-heptadiene, 4-bromo-1,6-octadiene, 3-chloro-4-methyl-1,6-octadiene, 4-bromo-7-methyl-1,6-octadiene, 4-chloro-1,7-octadiene, 3-chloro-4-methyl-1,7-octadiene, 4-bromo-1,7-nonadiene, 4-bromo-4-methyl-1,7-nonadiene, 4-bromo-1,8-nonadiene, 3-chloro-4-methyl-1,8-nonadiene, 5-bromo-1,8-decadiene, 3-chloro-5-methyl-1,8-decadiene, 5-bromo-1,9-decadiene, 3-chloro-5-methyl-1,9-decadiene, 5-bromo-1,10-undecadiene, and 5-bromo-1,1'-dodecadiene;

[0056] silane-containing dienes such as bis(vinyloxy)silane, dimethyl bis(vinyloxy)silane, bisallyloxy silane, dimethylbis(allyloxy)silane, di(3-butenyl)dimethyl silane, bis(3-butenyloxy)silane, dimethylbis(3-butenyloxy)silane, di(4-pentenyl)dimethyl silane, bis(4-pentenyl)dimethyl silane, bis(4-pentenyl)dimethyl silane, di(5-hexenyl)dimethylsilane, bis(5-hexenyloxy)silane, and bis(5-hexenyloxy)dimethylsilane;

[0057] ester-containing diene compounds such as 3-butenyl-4-pentenoate, 4-pentenyl-4-pentenoate, 4-methoxycarbonyl-1,7-octadiene, and 4-methoxycarbonyl-1,9-decadiene;

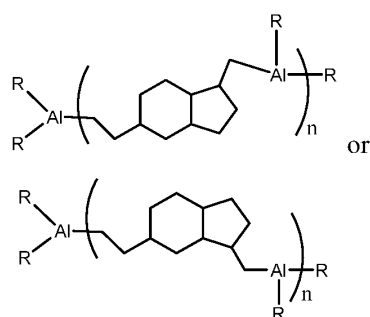
[0058] ether-containing diene compounds such as divinyl ether, diallyl ether, di(4-butenyloxy)ether, and di(5-hexenyloxy)ether; and

[0059] siloxy-containing diene compounds such as 4-trimethyl siloxymethyl-1,7-octadiene, and 4-trimethyl siloxymethyl-1,9-decadiene.

[0060] In further embodiments, Y is the derivative of conjugated diene compounds such as 1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 1-phenyl-1,3-butadiene, 1-phenyl-2,4-pentadiene, isoprene, 2-ethyl-1,3-butadiene, 2-propyl-1,3-butadiene, 2-butyl-1,3-butadiene, 2-pentyl-1,3-butadiene, 2-hexyl-1,3-butadiene, 2-heptyl-1,3-butadiene, 2-octyl-1,3-butadiene, and 2-phenyl-1,3-butadiene.

[0061] In further embodiments, Y is the derivative of a triene or a C₄ to C₁₀₀ hydrocarbon comprising three or more vinyl groups and optionally includes at least one heteroatom. In other words, the linking agent is a triene or a C₄ to C₁₀₀ hydrocarbon

comprising three or more vinyl groups and optionally includes at least one heteroatom. Suitable examples include but are not limited to 1,4,7-octatriene, 3-methyl-1,4,7-octatriene, 1,5,9-decatriene, 4-methyl-1,5,9-decatriene, 1,2,4-trivinylcyclohexane, and the like. In certain embodiments, the linking agent is 1,2,4-trivinylcyclohexane resulting in a composition of formula (I) having the following structural formulae with R as defined herein:



[0062] All linking groups discussed herein are generally available or can be produced by known methods.

Polymerization Process

[0063] In certain embodiments, the composition of formula (I) can function as a chain shuttling agent or a chain transfer agent during an olefin polymerization process.

[0064] Accordingly, the present disclosure relates to a polymerization process for the polymerization of at least one addition polymerizable monomer (i.e., olefin monomer) to form a polymer composition, the process comprising: contacting at least one addition polymerizable monomer (olefin monomer) with a catalyst composition under polymerization conditions; wherein the catalyst composition comprises the contact product (reaction product) of at least one catalyst precursor, an optional co-catalyst, and the composition of formula (I).

[0065] The capped dual-headed organoaluminum compositions of formula (I) and catalyst systems using the compositions of formula (I) described herein are suitable for use in any prepolymerization and/or polymerization process over a wide range of temperatures and pressures. Such temperatures and pressures, as well as other polymerization process information, described herein can be referred to as “polymerization conditions.” The temperatures may be in the range of from 50 °C to about 280 °C, preferably from 50 °C to about 200 °C. In another embodiment, the

polymerization temperature is above 0 °C, above 50 °C, above 80 °C, above 100 °C, above 150 °C or above 200 °C. In an embodiment, the pressures employed may be in the range from 1 atmosphere to about 500 atmospheres or higher. Polymerization processes include solution, gas phase, slurry phase and a high pressure process or a combination thereof.

[0066] In one embodiment, the present disclosure is directed toward a solution, high pressure, slurry or gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, preferably 2 to 12 carbon atoms, and more preferably 2 to 8 carbon atoms. The present disclosure is particularly directed to the polymerization of two or more olefin monomers of ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-decene. Useful monomers include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene. In another embodiment of the polymerization process of the present disclosure, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, and most preferably from 4 to 8 carbon atoms, is polymerized in a solution process. In another embodiment of the process of the present disclosure, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

[0067] In one aspect of this disclosure, there is provided a polymerization process and the resulting polymer, the process comprising polymerizing one or more olefin monomers in the presence of an olefin polymerization catalyst and the composition of formula (I) in a polymerization reactor or zone thereby causing the formation of at least some quantity of a polymer joined with the remnant of the composition of formula (I). Exemplary, non-limiting polymerization processes include those known in the art, those disclosed in U.S. Patent No. 8,501,885 B2, as well as those known in the art for producing random copolymers. Exemplary, non-limiting polymerization processes include those conducted in a single reactor or two reactors (parallel or series).

[0068] In yet another aspect, there is provided a process and the resulting polymer, the process comprising polymerizing one or more olefin monomers in the presence of an olefin polymerization catalyst and the composition of formula (I) in a polymerization reactor or zone thereby causing the formation of at least some quantity of an initial polymer joined with the remnant of the composition of formula (I) within the reactor or zone; discharging the reaction product from the first reactor or zone to a second polymerization reactor or zone operating under polymerization conditions that are distinguishable from those of the first polymerization reactor or zone; transferring at least some of the initial polymer joined with the remnant of the composition of formula (I) to an active catalyst site in the second polymerization reactor or zone by means of at least one remaining shuttling site of the composition of formula (I); and conducting polymerization in the second polymerization reactor or zone so as to form a second polymer segment bonded to some or all of the initial polymer by means of a remnant of the composition of formula (I), the second polymer segment having distinguishable polymer properties from the initial polymer segment.

[0069] During the polymerization, the reaction mixture is contacted with the activated catalyst composition according to any suitable polymerization conditions. The process can be generally characterized by use of elevated temperatures and pressures. Hydrogen may be employed as a chain transfer agent for molecular weight control according to known techniques, if desired. As in other similar polymerizations, it is generally desirable that the monomers and solvents employed be of sufficiently high purity that catalyst deactivation or premature chain termination does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressure, contacting with molecular sieves or high surface area alumina, or a combination of the foregoing processes may be employed.

[0070] Supports may be employed in the present methods, especially in slurry or gas-phase polymerizations. Suitable supports include solid, particulated, high surface area, metal oxides, metalloid oxides, or mixtures thereof (interchangeably referred to herein as an inorganic oxide). Examples include, but are not limited to talc, silica, alumina, magnesia, titania, zirconia, Sn_2O_3 , aluminosilicates, borosilicates, clays, and any combination or mixture thereof. Suitable supports preferably have a surface area as determined by nitrogen porosimetry using the B.E.T. method from 10 to 1000 m^2/g ,

and preferably from 100 to 600 m²/g. The average particle size typically is from 0.1 to 500 µm, preferably from 1 to 200 µm, more preferably 10 to 100 µm.

[0071] In one aspect of the present disclosure, the catalyst and optional support may be spray dried or otherwise recovered in solid, particulated form to provide a composition that is readily transported and handled. Suitable methods for spray drying a liquid containing slurry are well known in the art and usefully employed herein. Preferred techniques for spray drying catalyst compositions for use herein are described in U.S. Pat. Nos. 5,648,310 and 5,672,669.

[0072] The polymerization is desirably carried out as a continuous polymerization, for example, a continuous, solution polymerization, in which catalyst components, monomers, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to one or more reactors or zones and polymer product continuously removed therefrom. Within the scope of the terms “continuous” and “continuously” as used in this context include those processes in which there are intermittent additions of reactants and removal of products at small regular or irregular intervals, so that, over time, the overall process is substantially continuous. The composition of formula (I) (if used) may be added at any point during the polymerization including in the first reactor or zone, at the exit or slightly before the exit of the first reactor, between the first reactor or zone and any subsequent reactor or zone, or even solely to the second reactor or zone. If there exists any difference in monomers, temperatures, pressures or other polymerization conditions within a reactor or between two or more reactors or zones connected in series, polymer segments of differing composition such as comonomer content, crystallinity, density, tacticity, regio-regularity, or other chemical or physical differences, within the same molecule can be formed in the polymers of this disclosure. In such event, the size of each segment or block is determined by the polymer reaction conditions and typically is a most probable distribution of polymer sizes.

[0073] If multiple reactors are employed, each can be independently operated under high pressure, solution, slurry, or gas phase polymerization conditions. In a multiple zone polymerization, all zones operate under the same type of polymerization, such as solution, slurry, or gas phase, but, optionally, at different process conditions. For a solution polymerization process, it is desirable to employ homogeneous dispersions of

the catalyst components in a liquid diluent in which the polymer is soluble under the polymerization conditions employed. One such process utilizing an extremely fine silica or similar dispersing agent to produce such a homogeneous catalyst dispersion wherein normally either the metal complex or the co-catalyst is only poorly soluble is disclosed in U.S. Pat. No. 5,783,512. A high pressure process is usually carried out at temperatures from 100° C. to 400° C. and at pressures above 500 bar (50 MPa). A slurry process typically uses an inert hydrocarbon diluent and temperatures of from 0° C. up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerization medium. For example, typical temperatures in a slurry polymerization are from 30° C., generally from 60° C. up to 115° C., including up to 100° C., depending on the polymer being prepared. Pressures typically range from atmospheric (100 kPa) to 500 psi (3.4 MPa).

[0074] In all of the foregoing processes, continuous or substantially continuous polymerization conditions generally are employed. The use of such polymerization conditions, especially continuous, solution polymerization processes, allows the use of elevated reactor temperatures which results in the economical production of the present block copolymers in high yields and efficiencies.

[0075] The catalyst may be prepared as a homogeneous composition by addition of the requisite metal complex or multiple complexes to a solvent in which the polymerization will be conducted or in a diluent compatible with the ultimate reaction mixture. The desired co-catalyst or activator and, optionally, a composition of formula (I) may be combined with the catalyst composition either prior to, simultaneously with, or after combination of the catalyst with the monomers to be polymerized and any additional reaction diluent. Desirably, if present, the composition of formula (I) is added at the same time.

[0076] At all times, the individual ingredients as well as any active catalyst composition are protected from oxygen, moisture, and other catalyst poisons. Therefore, the catalyst components, the composition of formula (I), and activated catalysts are prepared and stored in an oxygen and moisture free atmosphere, generally under a dry, inert gas such as nitrogen.

[0077] Without limiting in any way the scope of the disclosure, one means for carrying out such a polymerization process is as follows. In one or more well stirred tank or

loop reactors operating under solution polymerization conditions, the monomers to be polymerized are introduced continuously together with any solvent or diluent at one part of the reactor. The reactor contains a relatively homogeneous liquid phase composed substantially of monomers together with any solvent or diluent and dissolved polymer. Preferred solvents include C₄₋₁₀ hydrocarbons or mixtures thereof, especially alkanes such as hexane or mixtures of alkanes, as well as one or more of the monomers employed in the polymerization. Examples of suitable loop reactors and a variety of suitable operating conditions for use therewith, including the use of multiple loop reactors, operating in series, are found in U.S. Pat. Nos. 5,977,251, 6,319,989 and 6,683,149.

[0078] Catalyst along with co-catalyst and the composition of formula (I) are continuously or intermittently introduced in the reactor liquid phase or any recycled portion thereof at a minimum of one location. The reactor temperature and pressure may be controlled, for example, by adjusting the solvent/monomer ratio or the catalyst addition rate, as well as by use of cooling or heating coils, jackets or both. The polymerization rate can be controlled by the rate of catalyst addition. The content of a given monomer in the polymer product is influenced by the ratio of monomers in the reactor, which is controlled by manipulating the respective feed rates of these components to the reactor. The polymer product molecular weight is controlled, optionally, by controlling other polymerization variables such as the temperature, monomer concentration, or by the previously mentioned composition of formula (I), or a chain terminating agent such as hydrogen, as is known in the art.

[0079] In one aspect of the disclosure, a second reactor is connected to the discharge of a first reactor, optionally by means of a conduit or other transfer means, such that the reaction mixture prepared in the first reactor is discharged to the second reactor without substantial termination of polymer growth. Between the first and second reactors, a differential in at least one process condition may be established. Generally, for use in formation of a copolymer of two or more monomers, the difference is the presence or absence of one or more comonomers or a difference in comonomer concentration. Additional reactors, each arranged in a manner similar to the second reactor in the series may be provided as well. Further polymerization is ended by contacting the

reactor effluent with a catalyst kill agent such as water, steam or an alcohol or with a coupling agent if a coupled reaction product is desired.

[0080] The resulting polymer product is recovered by flashing off volatile components of the reaction mixture such as residual monomer(s) or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder. In a continuous process the mean residence time of the catalyst and polymer in the reactor generally is from 5 minutes to 8 hours, for example, from 10 minutes to 6 hours.

[0081] In a further aspect of this disclosure, alternatively, the foregoing polymerization may be carried out in a plug flow reactor optionally with a monomer, catalyst, the composition of formula (I), temperature or other gradient established between differing zones or regions thereof, further optionally accompanied by separate addition of catalysts and/or the composition of formula (I), and operating under adiabatic or non-adiabatic polymerization conditions.

[0082] The use of functionalized derivatives of polymers are also included within the present disclosure. Examples include polymers with Al termini resulting from the composition of formula (I). Because a substantial fraction of the polymeric product exiting the reactor is terminated with metal, further functionalization is relatively easy. The metallated polymer species can be utilized in well-known chemical reactions such as those suitable for other alkyl-aluminum compounds to form amine-, hydroxy-, epoxy-, silane, vinylic, and other functionalized terminated polymer products. Polymers with Al termini can also be functionalized via thermal elimination of a di-unsaturated polymer by heating the Al-terminated polymer to temperatures causing beta-hydride elimination, preferably to 150 – 250 °C in the presence of sacrificial monomer, such as ethylene, which reacts with the resulting aluminum-hydride species, preventing the eliminated di-unsaturated polymer from undergoing the reverse reaction (i.e. insertion into the aluminum-hydride species).

Olefin Monomers

[0083] Suitable monomers for use in preparing the polymer products of the present disclosure in polymerization processes include any addition polymerizable monomer, generally any olefin or diolefin monomer. Suitable monomers can be linear, branched, acyclic, cyclic, substituted, or unsubstituted. In one aspect, the olefin can be any α -

olefin, including, for example, ethylene and at least one different copolymerizable comonomer, propylene and at least one different copolymerizable comonomer having from 4 to 20 carbons, or 4-methyl-1-pentene and at least one different copolymerizable comonomer having from 4 to 20 carbons. Examples of suitable monomers include, but are not limited to, straight-chain or branched α -olefins having from 2 to 30 carbon atoms, from 2 to 20 carbon atoms, or from 2 to 12 carbon atoms. Specific examples of suitable monomers include, but are not limited to, ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexane, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene. Suitable monomers for use in preparing the copolymers disclosed herein also include cycloolefins having from 3 to 30, from 3 to 20 carbon atoms, or from 3 to 12 carbon atoms. Examples of cycloolefins that can be used include, but are not limited to, cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene. Suitable monomers for preparing the copolymers disclosed herein also include di- and poly-olefins having from 3 to 30, from 3 to 20 carbon atoms, or from 3 to 12 carbon atoms. Examples of di- and poly-olefins that can be used include, but are not limited to, butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylidene norbornene, vinyl norbornene, dicyclopentadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene. In a further aspect, aromatic vinyl compounds also constitute suitable monomers for preparing the copolymers disclosed here, examples of which include, but are not limited to, mono- or poly-alkylstyrenes (including styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene and p-ethylstyrene), and functional group-containing derivatives, such as methoxystyrene, ethoxystyrene, vinylbenzoic acid, methyl vinylbenzoate, vinylbenzyl acetate, hydroxystyrene, o-chlorostyrene, p-chlorostyrene, divinylbenzene, 3-phenylpropene, 4-phenylpropene and α -methylstyrene, vinylchloride, 1,2-difluoroethylene, 1,2-dichloroethylene, tetrafluoroethylene, and 3,3,3-trifluoro-1-propene, provided the monomer is polymerizable under the conditions employed.

[0084] Further, in one aspect, suitable monomers or mixtures of monomers for use in combination with the composition of formula (I) disclosed here include ethylene; propylene; mixtures of ethylene with one or more monomers selected from propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, and styrene; and mixtures of ethylene, propylene and a conjugated or non-conjugated diene. In this aspect, the copolymer or interpolymer can contain two or more intramolecular regions comprising differing chemical or physical properties, especially regions of differentiated comonomer incorporation, joined in a dimeric, linear, branched or polybranched polymer structure. Such polymers may be prepared by altering the polymerization conditions during a polymerization that includes a composition of formula (I), for example by using two reactors with differing comonomer ratios, multiple catalysts with differing comonomer incorporation abilities, or a combination of such process conditions, and optionally a polyfunctional coupling agent.

Polymer Products

[0085] As disclosed herein, the polymer products refer to polymer products, after polymerization that are typically subjected to chemical treatment to consume reactive metal alkyl groups and liberate the polymer products from attachment to transition group or main group metals. This process comprises hydrolysis with water to generate saturated polymer end groups. Alternatively, addition of various organic or inorganic reagents may be added to both consume the metal alkyl groups and generate reactive functional end groups on the polymer chains.

[0086] The polymers produced by the processes of the present disclosure can be used in a wide variety of products and end-use applications. The polymers produced can be homo- and co-polymers of ethylene and propylene and include linear low density polyethylene, elastomers, plastomers, high-density polyethylenes, medium density polyethylenes, low density polyethylenes, polypropylene, and polypropylene copolymers. Propylene based polymers produced include isotactic polypropylene, atactic polypropylene, and random, block or impact copolymers.

[0087] Utilizing the polymerization processes disclosed here, novel polymer compositions, including block copolymers of one or more olefin monomers having the present molecular weight distribution, are readily prepared. Exemplary polymers comprise in polymerized form at least one monomer selected from ethylene, propylene,

and 4-methyl-1-pentene. Illustratively, the polymers are interpolymers comprising in polymerized form ethylene, propylene, or 4-methyl-1-pentene and at least one different C2-20 α -olefin comonomer, and optionally one or more additional copolymerizable comonomers. Suitable comonomers are selected from diolefins, cyclic olefins, and cyclic diolefins, halogenated vinyl compounds, vinylidene aromatic compounds, and combinations thereof. Exemplary polymers are interpolymers of ethylene with propylene, 1-butene, 1-hexene or 1-octene. Illustratively, the polymer compositions disclosed here have an ethylene content from 1 to 99 percent, a diene content from 0 to 10 percent, and a styrene and/or C3-8 α -olefin content from 99 to 1 percent, based on the total weight of the polymer. The polymers of the present disclosure may have a weight average molecular weight (M_w) from 500 to 2,500,000 in accordance with conventional GPC methods. Typically, the polymers of the present disclosure have a weight average molecular weight (M_w) from 500 to 250,000 (e.g., from 2,000 to 150,000, from 3,000 to 100,000, from 1,000 to 25,000, from 5,000 to 25,000, etc.) in accordance with conventional GPC methods.

[0088] The polymers prepared according to this disclosure can have a melt index, I2, from 0.01 to 2000 g/10 minutes, typically from 0.01 to 1000 g/10 minutes, more typically from 0.01 to 500 g/10 minutes, and especially from 0.01 to 100 g/10 minutes in accordance with ASTM D-792, Method B. Desirably, the disclosed polymers can have molecular weights, M_w , from 1,000 g/mol to 5,000,000 g/mol, typically from 1000 g/mol to 1,000,000 g/mol, more typically from 1000 g/mol to 500,000 g/mol, and especially from 1,000 g/mol to 300,000 g/mol in accordance with conventional GPC methods.

[0089] The density of the polymers of this disclosure can be from 0.80 to 0.99 g/cc and typically, for ethylene containing polymers, from 0.85 g/cc to 0.97 g/cc (e.g., from 0.853 to 0.970 g/cc), in accordance with ASTM D-792, Method B.

[0090] The polymers according to this disclosure may be differentiated from conventional, random copolymers, physical blends of polymers, and block copolymers prepared via sequential monomer addition, fluxional catalysts, or by anionic or cationic living polymerization techniques, by, among other things, their narrow molecular weight distributions. In this aspect, for example, the polymer composition prepared according to this disclosure can be characterized by a polydispersity index (PDI) of

from 1.5 to 10.0 (e.g, from 2.0 to 8.0, from 2.0 to 6.0, from 2.0 to 5.0, from 2.0 to 4.0, etc.). For example, the polydispersity index (PDI) of the polymer composition can be from 1.5 to 2.8, from 1.5 to 2.5, or from 1.5 to 2.3.

[0091] If present, the separate regions or blocks within each polymer are relatively uniform, depending on the uniformity of reactor conditions, and chemically distinct from each other. That is, the comonomer distribution, tacticity, or other property of segments within the polymer are relatively uniform within the same block or segment. However, the average block length can be a narrow distribution, but is not necessarily so. The average block length can also be a most probable distribution.

[0092] Illustratively, these interpolymers can be characterized by terminal blocks or segments of polymer having higher tacticity or crystallinity from at least some remaining blocks or segments. Illustratively, the polymer can be a triblock copolymer containing a central polymer block or segment that is relatively amorphous or even elastomeric.

[0093] In a still further aspect of this disclosure, there is provided a polymer composition comprising: (1) an organic or inorganic polymer, preferably a homopolymer of ethylene or of propylene and/or a copolymer of ethylene or propylene with one or more copolymerizable comonomers, and (2) a polymer or combination of polymers according to the present disclosure or prepared according to the process disclosed here.

[0094] The polymer products include combinations of two or more polymers comprising regions or segments (blocks) of differing chemical composition. In addition, at least one of the constituents of the polymer combination can contain a linking group which is the remnant of the composition of formula (I), causing the polymer to possess certain physical properties.

[0095] Various additives may be usefully incorporated into the present compositions in amounts that do not detract from the properties of the resultant composition. These additives include, for example, reinforcing agents, fillers including conductive and non-conductive materials, ignition resistant additives, antioxidants, heat and light stabilizers, colorants, extenders, crosslinkers, blowing agents, plasticizers, flame retardants, anti-drip agents, lubricants, slip additives, anti-blocking aids, anti-degradants, softeners, waxes, pigments, and the like, including combinations thereof.

[0096] The resultant polymers may be block interpolymers that can be characterized by an average block index, e.g., as discussed in U.S. Patent Nos. 7,947,793, 7,897,698, and 8,293,859. The resultant polymers may be block composites that can be characterized by a block composite index, e.g., as discussed in U.S. Patent Nos. 8,563,658, 8,476,366, 8,686,087, and 8,716,400. The resultant polymers may be crystalline block composites that can be characterized by a crystalline block composite index, e.g., as discussed in U.S. Patent Nos. 8,785,554, 8,822,598, and 8,822,599. The resultant polymers may be specified block composites that can be characterized by a microstructure index, e.g., as discussed in WO 2016/028957. The resultant polymers may be specified block composites that can be characterized by a modified block composite index, e.g., as discussed in WO 2016/028970.

[0097] In certain embodiments, the process for preparing the composition of formula (I) may be combined with functionalization chemistry to develop telechelic polymers. In certain embodiments, the composition of formula (I) can generate and grow telechelic polymer chains with both ends bonded to the composition of formula (I); subsequent transformation of the terminal polymeryl-metal bonds to desired di-end-functional groups may then occur to form the telechelic polymer.

[0098] Applications of the combination of the process for preparing the composition of formula (I) of the present disclosure with functionalization chemistry are in no way limited to development of telechelic polymers and the above example. In certain embodiments, the process for preparing the composition of formula (I) of the present disclosure may be combined with, e.g., coordinative chain transfer polymerization, to produce functionalized polyolefins.

[0099] The polymers of the present disclosure may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, isotactic polypropylene, ethylene propylene copolymers and the like.

[0100] Polymers produced by the process of the present disclosure and blends thereof are useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding, roto-molding. Films include

blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing film or oriented films.

EXAMPLES

Methods

[0101] ¹H NMR: ¹H NMR spectra are recorded on a Bruker AV-400 spectrometer at ambient temperature. ¹H NMR chemical shifts in benzene-*d*₆ are referenced to 7.16 ppm (C₆D₅H) relative to TMS (0.00 ppm).

[0102] ¹³C NMR: ¹³C NMR spectra of polymers are collected using a Bruker 400 MHz spectrometer equipped with a Bruker Dual DUL high-temperature CryoProbe. The polymer samples are prepared by adding approximately 2.6g of a 50/50 mixture of tetrachloroethane-*d*₂/orthodichlorobenzene containing 0.025M chromium trisacetylacetonate (relaxation agent) to 0.2 g of polymer in a 10mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150 °C. The data is acquired using 320 scans per data file, with a 7.3 second pulse repetition delay with a sample temperature of 120 °C.

[0103] GC/MS: Tandem gas chromatography/low resolution mass spectroscopy using electron impact ionization (EI) is performed at 70 eV on an Agilent Technologies 6890N series gas chromatograph equipped with an Agilent Technologies 5975 inert XL mass selective detector and an Agilent Technologies Capillary column (HP1MS, 15m X 0.25mm, 0.25 micron) with respect to the following:

Programed method:
Oven Equilibration Time 0.5 min
50 °C for 0 min
then 25 °C/min to 200 °C for 5 min
Run Time 11 min

[0104] GPC: The gel permeation chromatographic system consists of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140 °C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160 °C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

[0105] Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000 and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80 °C. with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):
$$M_{\text{polyethylene}} = 0.431(M_{\text{polystyrene}})$$

Polyethylene equivalent molecular weight calculations are performed using Viscotek TriSEC software Version 3.0.

[0106] Molecular Weight: Molecular weights are determined by optical analysis techniques including deconvoluted gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) as described by Rudin, A., “Modern Methods of Polymer Characterization”, John Wiley & Sons, New York (1991) pp. 103-112.

Materials

[0107] Performance of all examples discussed herein is under an inert atmosphere using dry box techniques unless otherwise stated.

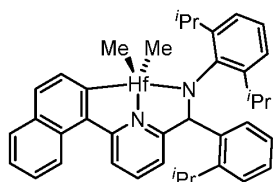
[0108] The following materials are obtained from Sigma-Aldrich and purified as needed prior to use: diisobutylaluminum hydride (DIBAL-H); triisobutylaluminum (TIBA); 5-ethylidene-2-norbornene (ENB); cyclohexene; divinylbenzene; 1,9-decadiene; 1,4-pentadiene; 1,3-butadiene; *p*-xylene; C₆D₆; 4-tert-butylcatechol; toluene; methanol; divinylchlorosilane; diethylether; phenylmagnesium bromide; hexane; divinylphenylsilane; divinylmethylsilane; THF; vinylmagnesium bromide; benzene; pentane; D₂O; BHT-benzoic acid; and pentamethylenebis(magnesium bromide).

[0109] 1,4-bis(chlorodimethylsilyl)benzene and 1,5-bis(dimethyl(vinyl)silyl)pentane are obtained from Alfa Aesar.

[0110] Isopar™ E is obtained from ExxonMobil Chemical Company.

[0111] The activator $[\text{HNMe}(\text{C}_{18}\text{H}_{37})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ("Activator A") is obtained from Boulder Scientific Co.

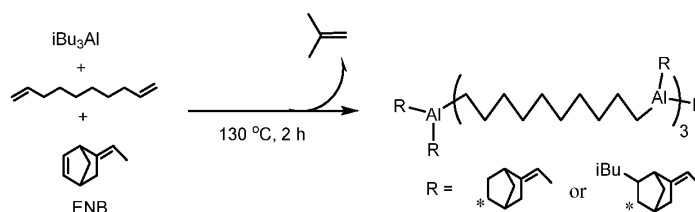
[0112] The catalyst $[\text{N}-(2,6\text{-di}(1\text{-methylethyl})\text{phenyl})\text{amido})(2\text{-isopropylphenyl})(\alpha\text{-naphthalen-2-yl})(6\text{-pyridin-2-yl})\text{methane}]\text{hafnium dimethyl}$ ("Catalyst A") having the structure shown below is prepared according to the teachings of WO 03/40195 and WO 04/24740 as well as methods known in the art.



[0113] MMAO-3A is obtained from Akzo Nobel.

Example 1

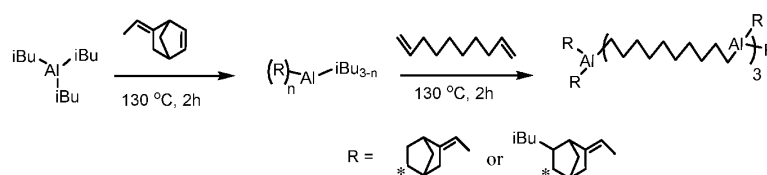
[0114] Preparation of capped dual-headed organoaluminum composition using TIBA, ENB and 1,9-decadiene: In a nitrogen-filled drybox, TIBA (2.0 mL, 7.9 mmol), 1,9-decadiene (1.1 mL, 5.94 mmol), and ENB (1.6 mL, 11.89 mmol) are mixed in 3.5 mL of *p*-xylene in a scintillation vial with a stir-bar. This mixture is heated to and held at 130 °C with stirring for two hours, and a small needle is inserted through the septum cap for venting. After two hours, the mixture is clear and viscous, and samples are taken for ^1H NMR and GC/MS (after quenching with water). As seen in FIG. 1, ^1H NMR in C_6D_6 shows that the intended reaction (see non-limiting Reaction Scheme 1) is complete (all vinyl groups are consumed) and the capped dual-headed organoaluminum composition is formed. As seen in FIG. 2, GC/MS shows major peaks at m/z of 122, 142, and 178, which are consistent with the expected hydrolyzed products of the capped dual-headed organoaluminum composition.



Reaction Scheme 1.

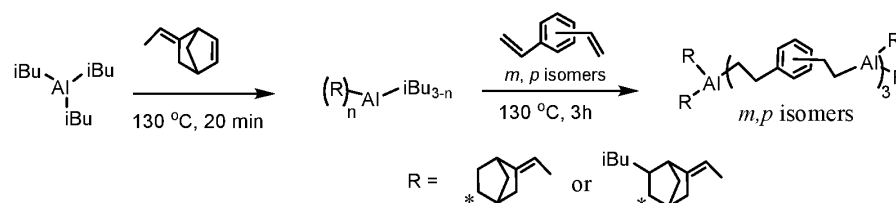
Example 2

[0115] Preparation of capped dual-headed organoaluminum composition using TIBA, ENB and 1,9-decadiene: In a nitrogen-filled drybox, ENB (1.6 mL, 11.9 mmol) and TIBA (2.0 mL, 7.9 mmol) are mixed in 3.5 mL of *p*-xylene in a scintillation vial with a stir-bar. This mixture is heated to and held at 130 °C with stirring for two hours, and a small needle is inserted through the septum cap for venting. After two hours, a sample of the mixture (ca 0.1 mL) is taken and mixed with C₆D₆ (0.5 mL) for ¹H NMR (see FIG. 3A), which shows that all of ENB is consumed. Subsequently, 1,9-decadiene (1.1 mL, 5.94 mmol) is added to the mixture, and heating at 130 °C is continued with stirring for another two hours. Afterwards, the mixture is clear and viscous, and samples are taken for ¹H NMR and GC/MS (after quenching with water). As seen in FIG. 3B, ¹H NMR in C₆D₆ shows that the intended reaction (see non-limiting Reaction Scheme 2) is complete (all vinyl groups are consumed) and the capped dual-headed organoaluminum composition is formed. As seen in FIG. 4, GC/MS shows major peaks at *m/z* of 122, 142, and 178, which are consistent with the expected hydrolyzed products of the capped dual-headed organoaluminum composition.

**Reaction Scheme 2.****Example 3**

[0116] Preparation of capped dual-headed organoaluminum composition using TIBA, ENB and divinylbenzene: In a nitrogen-filled drybox, TIBA (3.14 mL, 12.46 mmol), ENB (2.80 mL, 20.77 mmol) are mixed in 7 mL of *p*-xylene in a scintillation vial with a stir-bar. This mixture is heated to and held at 130 °C while stirring for 20 minutes, and a small needle is inserted through the septum cap for venting. After 20 minutes, divinylbenzene (1.18 mL, 8.31 mmol, d 0.914, 2 equiv; 80%, mixture of *m/p* isomers, stab. with 1000 ppm 4-tert-butylcatechol) is added to the mixture, and heating at 130 °C is continued with stirring for three hours. The reaction proceeds as intended (see non-limiting Reaction Scheme 3) to form the dual-headed organoaluminum

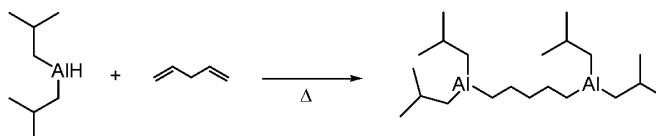
composition. The mixture is then allowed to cool to 25 °C. Samples are taken for GC/MS and, as seen in FIG. 5, the intended reaction is confirmed as the expected hydrolyzed products of the capped dual-headed organoaluminum composition are shown.



Reaction Scheme 3.

Example 4

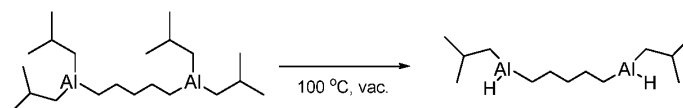
[0117] Preparation of (iBu)₂Al-(CH₂)₅-Al(iBu)₂: In a nitrogen-filled drybox, neat DIBAL-H (0.8 g, 5.63 mmol) and 1,4-pentadiene (0.291 mL, 2.81 mmol) are mixed in 3 mL of *p*-xylene in a scintillation vial with a stir-bar. This mixture is heated to and held at 50°C with stirring for 4.5 hours, then heated to and held at 60°C for 1 hour. The reaction proceeds as intended (see non-limiting Reaction Scheme 4). To confirm the reaction, a small aliquot is dissolved in C₆D₆, quenched with water, and analyzed by ¹H NMR. As seen in FIG. 6A, ¹H NMR shows the expected hydrolysis products (isobutene and pentane) of the intended reaction. *Note:* this reaction can also be carried out in toluene or neat.



Reaction Scheme 4.

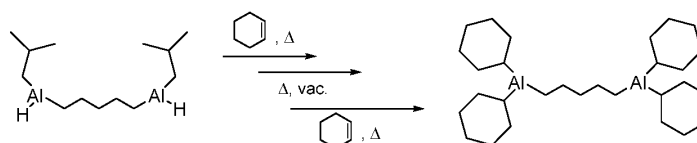
[0118] Preparation of (iBu)HAL-(CH₂)₅-AlH(iBu): In a nitrogen-filled drybox, ca 5 mL of (iBu)₂Al-(CH₂)₅-Al(iBu)₂ in *p*-xylene (0.88 M) is heated to and held at 100°C under vacuum for 14 hours. A trap vial is used in this process to capture high-boiling *p*-xylene, which otherwise would condense in the vacuum tubing. The reaction proceeds as intended (see non-limiting Reaction Scheme 5). To confirm the reaction, an aliquot is diluted with C₆D₆ and a portion of this solution is hydrolyzed with water.

^1H NMR spectra are recorded of the product (FIG. 6B) and hydrolyzed product (FIG. 6C). Al-H signals are observed in the ^1H NMR of the non-hydrolyzed sample (2.8-4.0 ppm). The ^1H NMR spectrum of the hydrolyzed sample shows the expected hydrolysis products, isobutane and pentane, of the intended reaction.



Reaction Scheme 5.

[0119] Preparation of capped dual-headed organoaluminum composition using (iBu)HAl-(CH₂)₅-AlH(iBu): In a nitrogen-filled drybox, neat (iBu)HAl-(CH₂)₅-AlH(iBu) (0.100 g, 0.42 mmol) is dissolved in 1.5 mL of toluene, and excess cyclohexene (1.0 mL, 9.87 mmol; d = 0.811) is added. The reaction mixture is heated to and held at 90 °C for 14 hours in a sealed vial. The reaction mixture is reduced to a clear oil under vacuum and heated to and held at 100°C under vacuum for 14 hours to generate partially capped, C5-linked Al-H. Then the material is dissolved in toluene (0.5 mL), and cyclohexene (0.5 mL, 4.99 mmol) is added. The reaction mixture is heated to and held at 90°C with stirring overnight in a sealed vial to complete the intended reaction (see non-limiting Reaction Scheme 6) to form the capped dual-headed organoaluminum composition.

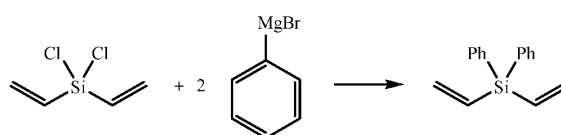


Reaction Scheme 6.

Example 5

[0120] Preparation of Divinyldiphenylsilane: A solution of phenylmagnesium bromide (30.18 mmol, 30 mL of 1.0 M in diethylether) is cooled in a glovebox freezer (-30 °C). A solution of divinyldichlorosilane (2.1 g, 13.72 mmol) in diethylether (10 mL) is then added slowly to the phenylmagnesium bromide. This mixture is allowed to stir overnight at room temperature, and the intended reaction (see non-limiting Reaction Scheme 7) proceeds. After the reaction period, the volatiles are removed, and the residue is extracted and filtered using hexane. The removal of the hexane results in an

oil with some cloudiness persisting. The mixture is re-filtered through a small pad of Celite using hexane as the eluent. Removal of the hexane results in the isolation of the desired product as a clear light yellow oil (2.75 g). Column chromatography is performed and results in the isolation of 1.01 g of purified product as a clear oil (1.0121 g, 31.2%). ^1H NMR (500 MHz, Benzene- d_6) δ 7.60 – 7.51 (m, 2H), 7.19 – 7.09 (m, 3H), 6.42 (dd, J = 20.2, 14.6 Hz, 1H), 6.08 (dd, J = 14.5, 3.7 Hz, 1H), 5.78 (dd, J = 20.3, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, Benzene- d_6) δ 136.08, 135.57, 134.19, 133.96, 129.42, 127.84.



Reaction Scheme 7.

[0121] Preparation of capped dual-headed organoaluminum composition using divinylldiphenylsilane: DIBAL-H (0.513g, 3.60 mmol) and ENB (0.722 g, 6.01 mmol) are mixed together neat in a glass tube. This mixture is heated to and held at 70 °C for 10 minutes, and then heated to and held at 130 °C for 10 minutes; a rubber septa with a needle is inserted to allow venting. After the reaction period, the tube is removed from the heat and cooled to room temperature. Then, divinylldiphenylsilane (0.568 g, 2.40 mmol) is added to the mixture. The rubber septa is replaced with a Teflon cap sealing the reaction vessel, and the mixture is then heated to and held at 130 °C for an additional 3 hours. After the reaction period, the mixture is cooled to room temperature resulting in a clear glassy material containing the capped dual-headed organoaluminum composition.

Example 6

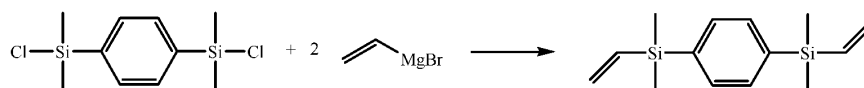
[0122] Preparation of capped dual-headed organoaluminum composition using divinylldimethylsilane: In a glass tube, DIBAL-H (0.7 g, 4.92 mmol) and ENB (0.986 g, 8.2 mmol) are mixed together neat. This mixture is heated to and held at 70 °C for 10 minutes, and then heated to and held at 130 °C for 10 minutes; a rubber septa with a needle is inserted to allow venting. After the reaction period, the tube is removed from the heat and cooled to room temperature. Subsequently, divinylldimethylsilane (0.368 g, 3.28 mmol) is added to the mixture, and the tube is sealed employing a Teflon cap. The mixture is then heated to and held at 70 °C for 5 minutes, and then heated to and

held at 80 °C for 5 minutes. This heating pattern is repeated with 10 °C increments until the desired temperature of 130 °C is reached. The mixture is then heated at 130 °C for an additional 3 hours. The mixture is then cooled to room temperature resulting in a clear viscous oil containing the capped dual-headed organoaluminum composition.

Example 7

[0123] Preparation of bis(dimethyl(vinyl)silyl)benzene: 1,4-

Bis(chlorodimethylsilyl)benzene (4.804 g, 18.24 mmol) in THF (40 mL) is cooled in a glovebox freezer (-30 °C). A solution of vinylmagnesium bromide (40.14 mmol, 40.14 mL of 1.0 M in THF) is then added slowly. This mixture is allowed to stir to room temperature overnight, and the intended reaction (see non-limiting Reaction Scheme 8) proceeds. After the reaction period, the volatiles are removed and the residue extracted and filtered using benzene. Removal of the benzene from the filtrate results in the isolation of a free flowing liquid as well as further precipitated salts. This material is filtered through a celite bed using hexane as the eluent. Removal of the volatiles results in the isolation of the desired product as a clear pale yellow liquid (3.5948 g, 79.9 %). ¹H NMR (500 MHz, Benzene-d₆) δ 7.51 (s, 4H), 6.30 – 6.19 (m, 1H), 5.99 – 5.91 (m, 1H), 5.69 (dd, J = 20.3, 3.8 Hz, 1H), 0.27 (s, 12H). ¹³C NMR (126 MHz, Benzene-d₆) δ 138.86, 137.74, 133.24, 132.59, -3.23.



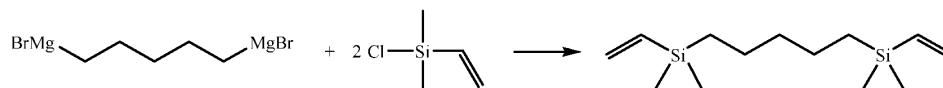
Reaction Scheme 8.

[0124] Preparation of capped dual-headed organoaluminum composition using

bis(dimethyl(vinyl)silyl)benzene: In a glass tube, DIBAL-H (1.5 g, 10.55 mmol) and ENB (2.113g, 17.58 mmol) are mixed together neat. This mixture is heated to and held at 70 °C for 10 minutes, and then heated to and held at 130 °C for 10 minutes; a rubber septa with a needle is inserted to allow venting. The tube is then cooled to room temperature. Subsequently, 1,4-bis(dimethyl(vinyl)silyl)benzene (1.733 g, 7.03 mmol) is added to the mixture. The rubber septa is replaced with a Teflon cap sealing the reaction vessel. The mixture is then heated to and held at 130 °C for an additional 3 hours. After the reaction period, the mixture is cooled to room temperature resulting in a clear glassy material containing the capped dual-headed organoaluminum composition.

Example 8

[0125] Preparation of 1,5-bis(dimethyl(vinyl)silyl)pentane: A solution of chlorodimethyl(vinyl)silane (2.654 g, 22 mmol) is diluted in THF (final volume 20 mL) and cooled in a glovebox freezer (-30 °C). Pentamethylenebis(magnesium bromide) (20 mL, 22 mmol, 1.0 M THF) is then added dropwise. The resulting mixture is allowed to stir for 3 hours at room temperature, and the intended reaction (see non-limiting Reaction Scheme 9) proceeds. After the reaction period, the volatiles are removed under vacuum. The residue comprised of copious gray salts is extracted using hexane and filtered. Removal of the volatiles results in the isolation of a slightly cloudy pale yellow oil. This oil is passed through a short silica gel plug using pentane. Removal of the pentane results in the isolation of the desired product as a clear light yellow oil (2.0873 g, 86.8 %). ¹H NMR (500 MHz, Benzene-*d*₆) δ 6.22 – 6.08 (m, 1H), 5.91 (dd, *J* = 14.6, 3.9 Hz, 1H), 5.65 (dd, *J* = 20.4, 3.8 Hz, 1H), 1.35 – 1.23 (m, 3H), 0.57 – 0.50 (m, 2H), 0.04 (s, 6H). ¹³C NMR (126 MHz, Benzene-*d*₆) δ 139.21, 131.21, 37.58, 23.75, 23.57, 15.28, -3.63.

**Reaction Scheme 9.**

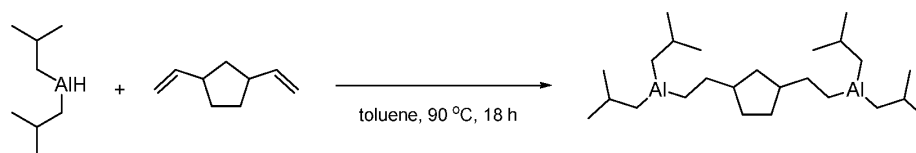
[0126] Preparation of capped dual-headed organoaluminum composition using 1,5-bis(dimethyl(vinyl)silyl)pentane: In a glass tube, DIBAL-H (3.08 g, 21.66 mmol) and ENB (4.339 g, 36.09 mmol) are mixed together neat. This mixture is heated to and held at 70 °C for 10 minutes, and then heated to and held at 130 °C for 10 minutes; a rubber septa with a needle is inserted to allow venting. After the reaction period, the tube is cooled to room temperature. Subsequently, 1,5-bis(dimethyl(vinyl)silyl)pentane (1.621 g, 14.44 mmol) is added to the mixture. The rubber septa is replaced with a Teflon cap sealing the reaction vessel. The mixture is then heated to and held at 130 °C for an additional 3 hours, with the mixture being white and cloudy and able to stir easily despite slight build-up of viscosity during the early portion of the reaction period. After the reaction period, the mixture is cooled to room temperature resulting in a viscous, milky material containing the capped dual-headed organoaluminum composition.

Example 9

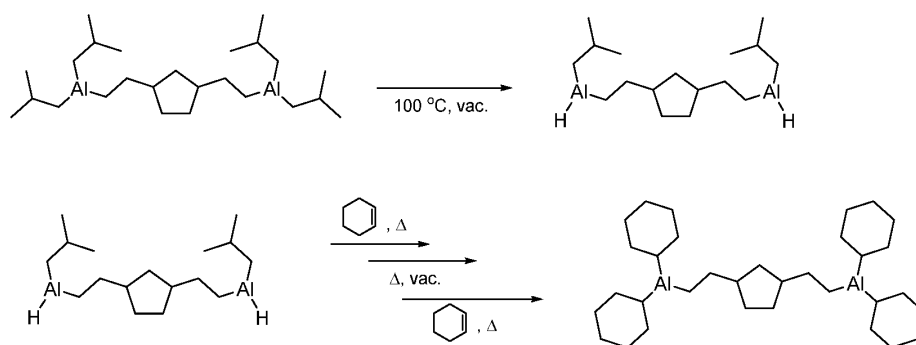
[0127] Preparation of $(\text{Cy})_2\text{Al}-(\text{CH}_2)_4-\text{Al}(\text{Cy})_2$: In a glass tube, 1,3-butadiene (24 mmol, 10 mL of 2.4 M in toluene) and DIBAL-H (6.827 g, 48 mmol) are mixed together. This mixture is heated to and held at 70 °C with stirring for a total of 32 hours. The mixture is then evaporated to dryness under vacuum, and full vacuum is continued overnight as the residue is heated to and held at 100 °C. After the reaction period, the residue is cooled back to room temperature. Subsequently, the residue is heated to and held at 80 °C in cyclohexene (40 mL) in a closed vessel overnight. Following the reaction period, the volatiles are removed resulting in the isolation of a thick oil. The residue is then heated to and held at 100 °C for 3 hours under full vacuum. After the reaction period, the residue is heated to and held at 80 °C in cyclohexene (30 mL) overnight. The volatiles are then removed, and the residue is again heated to and held at 100 °C under full vacuum for an additional 3 hours. After the reaction period, the residue is heated to and held at 80 °C in cyclohexene (30 mL) overnight. This process of heating at 80 °C in cyclohexane followed by 100 °C is repeated a total of 4 times. At this point, the volatiles are removed under vacuum resulting in the isolation of a sticky residue containing the capped dual-headed organoaluminum composition.

Example 10

[0128] Preparation of $(\text{iBu})_2\text{Al}-(\text{CH}_2)_2-\text{C}_5\text{H}_8-(\text{CH}_2)_2-\text{Al}(\text{iBu})_2$: In a nitrogen-filled drybox, neat DIBAL-H (1.00 mL, 5.61 mmol, $d=0.798$) and 1,3-divinylcyclopentane solution (30.9 wt% in toluene, 1.11 g, 2.81 mmol) are mixed in a capped scintillation vial with a stir-bar. This mixture is heated to and held at 90 °C with stirring for 18 hours. The reaction proceeds as intended (see non-limiting Reaction Scheme 10) to form the dual-headed organoaluminum composition. To confirm the reaction, an aliquot of the mixture is diluted with C_6D_6 , hydrolyzed with 10 wt% NaOD in D_2O , and analyzed by ^1H NMR and ^{13}C NMR. As seen in FIG. 5A and 5B, ^1H NMR and ^{13}C NMR show the expected hydrolysis product 1,3-bis(ethyl-2-d)cyclopentane of the dual-headed organoaluminum composition. The hydrolyzed sample is also analyzed by GC/MS, which shows a clean peak with m/z of 128 that is consistent with the expected hydrolyzed product of the dual-headed organoaluminum composition.

**Reaction Scheme 10.**

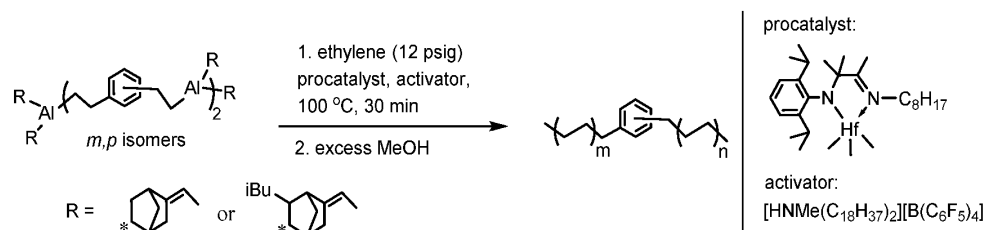
[0129] Preparation of $(\text{Cy})_2\text{Al}-(\text{CH}_2)_2-\text{C}_5\text{H}_8-(\text{CH}_2)_2-\text{Al}(\text{Cy})_2$. The title compound can be made following synthetic procedures shown in example 4 and non-limiting reaction scheme 11.

**Reaction Scheme 11.**

Polyethylene Polymerization

[0130] In a nitrogen-filled drybox, a vial equipped with a stir-bar is charged with Isopar™ E (10 mL) and Activator A (0.04 mL, 0.0024 mmol, 0.064 M). The vial is sealed with a septum cap and placed in a heating block set to 100 °C. An ethylene line (from a small cylinder) is connected and the vial headspace is slowly purged via a needle. The capped dual-headed organoaluminum composition prepared in Example 3 (0.37 mL, 0.30 mmol, 0.815 M based on divinylbenzene) and Procatalyst A (0.10 mL, 0.002 mmol, 0.02 M) are injected, and the purge needle is removed to maintain a total pressure at 12 psig. The reaction mixture is stirred for 30 min, then taken out of the drybox and quenched with MeOH (100 mL). The precipitated white polymer is stirred in methanol for 3 hours, followed by filtration and drying of the polymer under vacuum overnight (0.265 g). ^{13}C NMR shows the aromatic signals from the incorporated divinylbenzene and the saturated polymer chain ends (FIG. 7). GPC results: $M_n = 1,512$; $M_w = 3,880$; PDI = 2.57. The GPC chromatogram is shown in FIG. 8. This

exemplary polymerization of polyethylene is exemplified below in non-limiting Reaction Scheme 12.



Reaction Scheme 12.

Copolymer Polymerization in HOPR reactor

[0131] General HOPR Information: All chemicals used are either purchased as anhydrous reagents or thoroughly degassed before introduction into an MBraun drybox. All manipulations are performed while working in a nitrogen-filled drybox. Toluene, Isopar™ E, 1-octene, and ethylene gas are purified and dried by passing through a bed of Q-5 catalyst. All of the reactor chemistry is done using the HOPR equipped with a Xantus robotic workstation model 44 00 / 100. Both the liquid handler and reactor are installed in an MBraun drybox enabling liquid handling manipulations under an inert nitrogen atmosphere. The reagent solutions are made in the drybox prior to the experiment. The MMAO-3A are used either as the original stock 1.9 M solution or diluted with toluene. The 18 × 54 mm round bottom reactor tubes in the 24 well plate (4 × 6) are tared and weighed on the ABD weigh station. All reactor tubes are dried down using a Thermo Savant model SC250EXP for 10 hours at 80 °C. Heating of the reactor is done using a Mokon HTF system model H54124NR.

[0132] Representative HOPR Synthetic and Screening Procedure: A 24 well plate (4 × 6) with 18 × 54 mm round bottom reactor tubes is placed on the deck of the Tecan. To each reactor tube is added MMAO-3A (20 nmoles), Activator A (1.2 nmoles), 1-octene (100 µL), a capped dual-headed organoaluminum composition from a particular example (10 or 25 nmoles), and Isopar™ E (such that the final volume will be 5.0 mL). These reactor tubes are then placed into the HOPR which is at 20 °C with the lid secured. Then, magnetic stirring starts. The reactor is then pre-pressurized with 75 psi of ethylene gas. Next, the reactor is heated to the temperature of 100°C. The reactor is

then fully pressurized to 150 psi. Catalyst A (1 nmole) is then added to each reactor tube to initiate the polymerization. After 5 minutes, a BHT/Benzoic acid quench is added and then the reactor is cooled and slowly vented. The lid is removed and the tubes are placed back into the 4 × 6 rack to be dried down in the Savant and then weighed to obtain the mass of ethylene/octene copolymer produced followed by GPC analysis of the polymers. The polymerization data is presented below in Table 1.

Table 1.

Composition (Example #)	Composition Loading (micromoles)	Isolated Polymer (g)	M _w (g/mol)	M _n (g/mol)	PDI
None	0	0.087	2,139,010	472,460	4.53
3	25	0.277	85,080	23,910	3.56
3	25	0.153	115,080	19,610	5.87
3	25	0.317	76,800	21,140	3.63
5	10	0.268	82,880	31,030	2.67
5	25	0.284	50,660	20,260	2.50
5	25	0.316	49,630	17,190	2.89
6	10	0.300	40,530	17,580	2.30
6	10	0.293	39,250	16,410	2.39
6	25	0.263	24,240	9,610	2.52
6	25	0.255	21,750	8,730	2.49
7	10	0.118	402,110	68,090	5.91
7	10	0.123	307,640	24,760	12.42
7	25	0.142	257,080	23,190	11.09
7	25	0.143	256,340	16,880	15.18
8	10	0.214	82,970	30,910	2.68
8	10	0.197	85,970	29,620	2.90