CURABLE COMPOSITIONS COMPRISING UNSATURATED POLYOLEFINS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority to U.S. provisional application nos. 62/786084, 62/786100, 62/786119, and 62/786110, filed on December 28, 2018, which are incorporated herein by reference in their entirety.

FIELD

[0002] Embodiments relate to curable compositions that are useful for improved crosslinking.

BACKGROUND

[0003] Polyolefin elastomers, such as ethylene/alpha-olefin copolymers and olefin block copolymers, are widely used in cross-linked applications due to their ability to provide high mechanical performance, such as high resilience, softness, elasticity, and durability, among other things. However, polyolefin elastomers are sometimes limited in its processabilty usually having lower curing levels and poorer mechanical properties with a decrease in its molecular weight and lower viscosity of the polymer when it is desired to have higher flow and better processing. One approach to address this issue is to increase the amount of curing agent, such as peroxide, but such an approach is costly and leads to production of decomposition byproducts, which has an unpleasant odor. Accordingly, there is a need in the state of the art for novel polyolefin compositions that have higher processability and improved curing levels even with low amounts of curing agent and also have high mechanical performance. The present disclosure addresses this need.

SUMMARY

[0004] The present disclosure relates to a curable composition, the curable composition comprising (A) a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP and/or a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP; and (B) a curing component comprising a cross-linking agent, wherein:

L^1 at each occurrence independently is a polyolefin;

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

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

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

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

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

[0004a] In another aspect, the present disclosure relates to a crosslinked foam article made from a curable composition comprising (A) a polyolefin component comprising a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP; wherein the viscosity is a Brookfield viscosity (as measured at 177 °C) in accordance with ASTM-D3236 and (B) a curing component comprising a cross-linking agent, wherein:

L^1 is a polyolefin;

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

group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$;

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

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

A^2 is a hydrocarbyl group comprising a hindered double bond; and wherein the (A) polyolefin component is present in an amount of from 4 wt% to 15 wt%, based on the total weight of the curable composition.

[0004b] In another aspect, the present disclosure relates to a crosslinked foam article made from a curable composition comprising (A) a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP and a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP; wherein the viscosity is a Brookfield viscosity (as measured at 177 °C) in accordance with ASTM-D3236 and (B) a curing component comprising a cross-linking agent, wherein:

L^1 at each occurrence independently is a polyolefin;

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

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

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

A^2 is a hydrocarbyl group comprising a hindered double bond; and wherein the (A) polyolefin component is present in an amount of from 4 wt% to 15 wt%, based on the total weight of the curable composition.

[0005] The curable composition may further comprise (C) an additive component. The (C) additive component may comprise a UV stabilizer. Further, the (C) additive component may comprise a blowing agent. The curable composition may further comprise (D) at least one other polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

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

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

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

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

DETAILED DESCRIPTION

Definitions

[0010] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

[0011] 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.

[0012] The terms "comprising," "including," "having" and their derivatives are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, component, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step, or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step, or procedure not specifically delineated or listed. The term "or," unless stated otherwise, refers to the listed members individually as well as in any combination.

[0013] The term "hindered double bond" refers to a carbon-carbon double bond that cannot readily participate in coordination polymerization. In other words, a hindered double bond has negligible reactivity to participate in coordination polymerization. Examples of hindered double bonds include but are not limited to the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon. The term "hindered double bond," as defined herein, excludes the double bonds of strained cyclic olefins that can readily participate in coordination polymerization. As one of ordinary skill in the art would understand, examples of such strained cyclic olefins include but are not limited to norbornene, ethylidene norbornene (ENB), 5-vinyl-2-norbornene (VNB), dicyclopentadiene, norbornadiene, 5-methylene-2-norbornene (MNB), 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, etc. The term "hindered double bond," as defined herein, further excludes the double bond of a vinyl group attached to an unbranched alpha carbon.

[0014] The term "composition" refers to a mixture of materials or components which comprise the composition. Accordingly, the term "a composition comprising" and similar terms are not intended to exclude the presence of any additional components of the composition, whether or not the same is specifically disclosed.

[0015] The term "acyclic" refers to a series of atoms in a polymer or compound where such a series is linear or branched. Accordingly, the term "acyclic hydrocarbyl group" refers to a hydrocarbyl group that is linear or branched.

[0016] The term "cyclic" refers to a series of atoms in a polymer or compound where such a series includes one or more rings. Accordingly, the term "cyclic hydrocarbyl group" refers to a hydrocarbyl group that contains one or more rings. A "cyclic hydrocarbyl group," as used herein, may contain acyclic (linear or branched) portions in addition to the one or more rings.

[0017] The term "substituted" refers to a substitution of one or more hydrogen atoms with, for example, an alkyl group. The term "unsubstituted" refers to the absence of such a substitution.

[0018] The term "heteroatom," as one of ordinary skill in the art would understand, refers to any main group atom that is not carbon or hydrogen. Suitable heteroatoms include but are not limited to nitrogen, oxygen, sulfur, phosphorus, and the halogens.

[0019] As used herein, the terms "hydrocarbyl," "hydrocarbyl group," and like terms refer to compounds composed entirely of hydrogen and carbon, including aliphatic, aromatic, acyclic, cyclic, polycyclic, branched, unbranched, saturated, and unsaturated compounds.

[0020] The terms "hydrocarbyl," "hydrocarbyl group," "alkyl," "alkyl group," "aryl," "aryl group," "cycloalkene" and like terms are intended to include every possible isomer, including every structural isomer or stereoisomer. The same applies for like terms including but not limited to heterohydrocarbyl, hydrocarbylene, heterohydrocarbylene, alkylene, heteroalkyl, heteroalkylene, arylene, heteroaryl, heteroarylene, cycloalkyl, cycloalkylene, heterocycloalkyl, and heterocycloalkylene.

[0021] The term "endocyclic double bond" refers to a double bond between two carbon atoms that are members of a ring. The term "exocyclic double bond" refers to a double bond between two carbon atoms where only one of the carbon atoms is a member of a ring.

[0022] "Active catalyst," "active catalyst composition," and like terms refer to a transition metal compound that is, with or without a co-catalyst, capable of polymerization of unsaturated monomers. An active catalyst may be a "procatalyst" that becomes active to polymerize unsaturated monomers without a co-catalyst. Alternatively, an active catalyst may a "procatalyst" that becomes active, in combination with a co-catalyst, to polymerize unsaturated monomers.

[0023] The term "procatalyst" is used interchangeably with "catalyst," "precatalyst," "catalyst precursor," "transition metal catalyst," "transition metal catalyst precursor," "polymerization catalyst," "polymerization catalyst precursor," "transition metal complex," "transition metal compound," "metal complex," "metal compound," "complex," "metal-ligand complex," and like terms.

[0024] "Co-catalyst" refers to a compound that can activate certain procatalysts to form an active catalyst capable of polymerization of unsaturated monomers. The term "co-catalyst" is used interchangeably with "activator" 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" that refers to polymers prepared from only one type of monomer and the terms "interpolymer" or "copolymer" as defined herein. Trace amounts of impurities, for example, catalyst residues, may be incorporated into and/or within the polymer.

[0026] "Interpolymer" or "copolymer" refer to a polymer prepared by polymerizing at least two different types of monomers. These generic terms include both polymers prepared from two different types of monomers and polymers prepared from more than two different types of monomers (e.g., terpolymers, tetrapolymers, etc.). These generic terms embrace all forms of interpolymers or copolymers, such as random, block, homogeneous, heterogeneous, etc.

[0027] An "ethylene-based polymer" or "ethylene polymer" is a polymer that contains a majority amount (greater than 50 wt%) of polymerized ethylene, based on the weight of the polymer, and, optionally, may further contain polymerized units of at least one comonomer. An "ethylene-based interpolymer" is an interpolymer that contains, in polymerized form, a majority amount (greater than 50 wt%) of ethylene, based on the weight of the interpolymer, and further contains polymerized units of at least one comonomer. Preferably, the ethylene-based interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). An "ethylene homopolymer" is a polymer that comprises repeating units derived from ethylene but does not exclude residual amounts of other components.

[0028] A "propylene-based polymer" or "propylene polymer" is a polymer that contains a majority amount (greater than 50 wt%) of polymerized propylene, based on the weight of the polymer, and, optionally, may further contain polymerized units of at least one comonomer. A "propylene-based interpolymer" is an interpolymer that contains, in polymerized form, a majority amount (greater than 50 wt%) of propylene, based on the weight of the interpolymer, and further contains polymerized units of at least one comonomer. Preferably, the propylene-based interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). A "propylene homopolymer" is a polymer that comprises repeating units derived from propylene but does not exclude residual amounts of other components.

[0029] An "ethylene/alpha-olefin interpolymer" is an interpolymer that contains a majority amount (greater than 50 wt%) of polymerized ethylene, based on the weight of the interpolymer, and further contains polymerized units of at least one alpha-olefin. Preferably, the ethylene/alpha-olefin interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). An "ethylene/alpha-olefin copolymer" is a copolymer that contains a majority amount (greater than 50 wt%) of polymerized ethylene, based on the weight of the copolymer, and further contains polymerized units of an alpha-olefin. Preferably, the ethylene/alpha-olefin copolymer is a random copolymer (i.e., comprises a random distribution of its monomeric constituents).

[0030] A "propylene/alpha-olefin interpolymer" is an interpolymer that contains a majority amount (greater than 50 wt%) of polymerized propylene, based on the weight of the interpolymer, and further contains polymerized units of at least one alpha-olefin. Preferably, the propylene/alpha-olefin interpolymer is a random interpolymer (i.e., comprises a random distribution of its monomeric constituents). A "propylene/alpha-olefin copolymer" is an interpolymer that contains a majority amount (greater than 50 wt%) of polymerized propylene, based on the weight of the copolymer, and further contains polymerized units of an alpha-olefin. Preferably, the propylene/alpha-olefin copolymer is a random copolymer (i.e., comprises a random distribution of its monomeric constituents).

[0031] "Polyolefin" refers to a polymer produced from olefin monomers, where an olefin monomer (also called an alkene) is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond.

[0032] The terms "chain transfer agent component" and "chain transfer agent" as used herein, refers to a compound or mixture of compounds that is capable of causing reversible or irreversible polymeryl exchange with active catalyst sites. Irreversible chain transfer refers to a transfer of a growing polymer chain from the active catalyst to the chain transfer agent that results in termination of polymer chain growth. Reversible chain transfer refers to transfers of growing polymer chain back and forth between the active catalyst and the chain transfer agent.

[0033] The term "olefin block copolymer" or "OBC" refers to an ethylene/alpha-olefin multi-block interpolymer and includes ethylene and one or more copolymerizable alpha-olefin comonomers in polymerized form, characterized by multiple blocks or segments of two or more (preferably three or more) polymerized monomer units, the blocks or segments differing in chemical or physical properties. Specifically, the term "olefin block copolymer"

refers to a polymer comprising two or more (preferably three 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), region-regularity or region-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. Non-limiting examples of the olefin block copolymers of the present disclosure, as well as the processes for preparing the same, are disclosed in U.S. Patent Nos. 7,858,706 B2, 8,198,374 B2, 8,318,864 B2, 8,609,779 B2, 8,710,143 B2, 8,785,551 B2, and 9,243,090 B2, which are all incorporated herein by reference in their entirety.

[0034] The term "block composite" ("BC") refers to a polymer comprising three polymer components: (i) an ethylene-based polymer (EP) having an ethylene content from 10 mol% to 90 mol% (a soft copolymer), based on the total moles of polymerized monomer units in the ethylene-based polymer (EP); (ii) an alpha-olefin-based polymer (AOP) having an alpha-olefin content of greater than 90 mol% (a hard copolymer), based on the total moles of polymerized monomer units in the alpha-olefin-based polymer (AOP); and (iii) a block copolymer (diblock copolymer) having an ethylene block (EB) and an alpha-olefin block (AOB); wherein the ethylene block of the block copolymer is the same composition as the EP of component (i) of the block composite and the alpha-olefin block of the block copolymer is the same composition as the AOP of component (ii) of the block composite. Additionally, in the block composite, the compositional split between the amount of EP and AOP will be essentially the same as that between the corresponding blocks in the block copolymer. Non-limiting examples of the block composites of the present disclosure, as well as processes for preparing the same, are disclosed in U.S. Patent Nos. 8,686,087 and 8,716,400, which are incorporated herein by reference in their entirety.

[0035] The term "specified block composite" ("SBC") refers to a polymer comprising three polymer components: (i) an ethylene-based polymer (EP) having an ethylene content from 78

mol% to 90 mol% (a soft copolymer), based on the total moles of polymerized monomer units in the ethylene-based polymer (EP); (ii) an alpha-olefin-based polymer (AOP) having an alpha-olefin content of from 61 mol% to 90 mol% (a hard copolymer), based on the total moles of polymerized monomer units in the alpha-olefin-based polymer (AOP); and (iii) a block copolymer (diblock copolymer) having an ethylene block (EB) and an alpha-olefin block (AOB); wherein the ethylene block of the block copolymer is the same composition as the EP of component (i) of the specified block composite and the alpha-olefin block of the block copolymer is the same composition as the AOP of component (ii) of the specified block composite. Additionally, in the specified block composite, the compositional split between the amount of EP and AOP will be essentially the same as that between the corresponding blocks in the block copolymer. Non-limiting examples of the specified block composites of the present disclosure, as well as processes for preparing the same, are disclosed in WO 2017/044547, which is incorporated herein by reference in its entirety.

[0036] The term "crystalline block composite" ("CBC") refers to polymers comprising three components: (i) a crystalline ethylene based polymer (CEP) having an ethylene content of greater than 90 mol%, based on the total moles of polymerized monomer units in the crystalline ethylene based polymer (CEP); (ii) a crystalline alpha-olefin based polymer (CAOP) having an alpha-olefin content of greater than 90 mol%, based on the total moles of polymerized monomer units in the crystalline alpha-olefin based copolymer (CAOP); and (iii) a block copolymer comprising a crystalline ethylene block (CEB) and a crystalline alpha-olefin block (CAOB); wherein the CEB of the block copolymer is the same composition as the CEP of component (i) of the crystalline block composite and the CAOB of the block copolymer is the same composition as the CAOP of component (ii) of the crystalline block composite. Additionally, in the crystalline block composite, the compositional split between the amount of CEP and CAOP will be essentially the same as that between the corresponding blocks in the block copolymer. Non-limiting examples of the crystalline block composites of the present disclosure, as well as the processes for preparing the same, are disclosed in US Pat. No. 8,822,598 B2 and WO 2016/01028961 A1, which are incorporated herein by reference in its entirety.

[0037] The term “crystalline” refers to a polymer that possesses a first order transition or crystalline melting point (Tm) as determined by differential scanning calorimetry (DSC) or equivalent techniques. The term may be used interchangeably with the term

"semicrystalline." The term "amorphous" refers to a polymer lacking a crystalline melting point as determined by differential scanning calorimetry (DSC) or equivalent technique.

(A) Polyolefin Component

[0038] In certain embodiments, the curable composition of the present disclosure may comprise from 1 wt% to 25 wt% (such as from 1 wt% to 25 wt%, or from 2 wt% to 25 wt%, or from 4 wt% to 25 wt%, or from 1 wt% to 20 wt%, or from 1 wt% to 15 wt%, or from 1 wt% to 11 wt%) of the (A) polyolefin component, based on the total weight of the curable composition.

[0039] In certain embodiments, the (A) polyolefin component comprises an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP. In certain embodiments, the (A) polyolefin component comprises a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP. In further embodiments, the (A) polyolefin component comprises an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP and a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP. In further embodiments, the (A) polyolefin component comprises an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP and a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP, wherein the (A) polyolefin component comprises a ratio of the unsaturated polyolefin of the formula A^1L^1 to the telechelic polyolefin of the formula $A^1L^1L^2A^2$ of from 1:99 to 99:1, or from 10:90 to 90:10, or from 20:80 to 80:20, or from 30:70 to 70:30, or from 40:60 to 60:40, or 50:50. In the present disclosure, each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ is a high flow polyolefin such that they each have a viscosity less than 100,000 cP, or less than 70,000 cP, or less than 50,000 cP, and wherein they each have a viscosity greater than 500 cP, or greater than 1,000 cP, or greater than 5,000 cP.

[0040] In all embodiments described herein, the (A) polyolefin component is a high flow polyolefin component, such that the (A) polyolefin component has a viscosity less than 100,000 cP, or less than 70,000 cP, or less than 50,000 cP. Further, the high flow polyolefin component has a viscosity greater than 500 cP, or greater than 1,000 cP, or greater than 5,000 cP.

[0041] As further described with respect to (D), the curable composition further comprises polymers other than the high flow unsaturated polyolefin of the formula A^1L^1 and the high flow telechelic polyolefin of the formula $A^1L^1L^2A^2$, such as ethylene-based polymers.

Examples of ethylene-based polymers include but are not limited to ethylene/alpha-olefin copolymers, such as those available as ENGAGE™ from The Dow Chemical Company, and olefin block copolymers available as INFUSE™ from The Dow Chemical Company. These ethylene-based polymers have low or no unsaturations.

[0042] As one of ordinary skill in the art would understand in view of the formula $A^1L^1L^2A^2$, A^1 is covalently bonded to L^1 through a carbon-carbon single bond, L^1 is covalently bonded to L^2 through a carbon-carbon single bond, and L^2 is covalently bonded to A^2 through a carbon-carbon single bond. Accordingly, when it is stated herein that L^1 of the formula $A^1L^1L^2A^2$ is a polyolefin, it is understood that L^1 is a divalent polyolefinyl group (a polyolefin missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds. Likewise, when it is stated that L^1 of the formula $A^1L^1L^2A^2$ is a polymer, it is understood that L^1 is a divalent polymeryl group (a polymer missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds. For example, when it is stated that L^1 is an ethylene homopolymer, it is understood that L^1 is a divalent ethylene homopolymeryl group (an ethylene homopolymer missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds. As a further example, when it is stated that L^1 is an ethylene/alpha-olefin copolymer, it is understood that L^1 is a divalent ethylene/alpha-olefin copolymeryl group (an ethylene/alpha-olefin copolymer missing two hydrogens) that is covalently bonded to each of the A^1 and L^2 groups through carbon-carbon single bonds.

[0043] Similarly, as one of ordinary skill in the art would understand in view of the formula A^1L^1, A^1 is covalently bonded to L^1 through a carbon-carbon single bond. Accordingly, wherein it is stated herein that L^1 of the formula A^1L^1 is a polyolefin, it is understood that L^1 is a polyolefinyl group (a polyolefin missing one hydrogen) that is covalently bonded to the A^1 group through a carbon-carbon single bond.

[0044] L^1 at each occurrence independently is a polyolefin resulting from the coordination polymerization of unsaturated monomers (and comonomers). Examples of suitable monomers (and comonomers) include but are not limited to ethylene and alpha-olefins of 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 5-ethyl-1-nonene, 1-octadecene and 1-eicosene; conjugated or nonconjugated dienes, such as butadiene, isoprene,

4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,5-heptadiene, 1,6-heptadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, 1,9-decadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene, 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene, and mixed isomers of dihydromyrcene and dihydroocimene; norbornene and alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, 5-methylene-2-norbornene, 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, and norbornadiene; and aromatic vinyl compounds such as styrenes, mono or poly alkylstyrenes (including styrene, o-methylstyrene, t-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene and p-ethylstyrene).

[0045] L^1 may be linear (unbranched), branched, or cyclic. The presence or absence of branching in L^1, and the amount of branching (if branching is present), can vary widely and may depend on the desired processing conditions and the desired polymer properties. If branching is present in L^1, the branching may be short chain branching or long chain branching. Exemplary types of long chain branching that may be present in L^1 include but are not limited to T-type branching and H-type branching. Accordingly, in some embodiments, L^1 may comprise long chain branching. In other words, in some embodiments, L^1 may comprise one or more long chain branches, wherein each long chain branch optionally comprises an A^2 group as defined herein.

[0046] In some embodiments, the A^1 group of each of the formulas A^1L^1 and $A^1L^1L^2A^2$ correlates to the last inserted monomer or comonomer based on the coordination polymerization of monomers and comonomers to form L^1. Accordingly, the selection of the monomers and comonomers for the coordination polymerization of L^1 will indicate what the A^1 group and the Y^1 group may be. In some embodiments, the A^1 group is a vinyl group. In some embodiments, the A^1 group is a vinylidene group of the formula $CH_2=C(Y^1)–$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a vinylene group of the formula $Y^1CH=CH–$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a

mixture of a vinylidene group of the formula $CH_2=C(Y^1)–$ and a vinylene group of the formula $Y^1CH=CH–$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group. In some embodiments, the A^1 group is a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0047] In further embodiments, the A^1 group is a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, wherein A^1 comprises a ratio of the vinyl group to the vinylene group of the formula $Y^1CH=CH–$ of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0048] In further embodiments, the A^1 group is a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, wherein A^1 comprises a ratio of the vinyl group to the vinylidene group of the formula $CH_2=C(Y^1)–$ of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0049] In further embodiments, the A^1 group is a mixture of a vinylidene group of the formula $CH_2=C(Y^1)–$ and a vinylene group of the formula $Y^1CH=CH–$, wherein A^1 comprises a ratio of the vinylidene group of the formula $CH_2=C(Y^1)–$ to the vinylene group of the formula $Y^1CH=CH–$ of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0050] In further embodiments, the A^1 group is a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, wherein A^1 comprises a ratio of the vinyl group to the sum of the vinylene group of the formula $Y^1CH=CH–$, the vinylidene group of the formula $CH_2=C(Y^1)–$, and the vinyl group of from 0.99:0.01 to 0.01:0.99, and wherein Y^1 is a C_1 to C_{30} hydrocarbyl group.

[0051] In certain embodiments, L^1 is a homopolymer comprising units derived from one monomer. The monomer may be selected from any of the suitable monomers discussed previously. In further embodiments, L^1 is an ethylene homopolymer comprising units derived from ethylene. In further embodiments, L^1 is a propylene homopolymer comprising units derived from propylene.

[0052] In some embodiments, L^1 is an interpolymer comprising units derived from at least two different types of monomers, such as a monomer and a comonomer. Accordingly, in certain embodiments, L^1 is an interpolymer comprising units derived from a monomer and at least one comonomer that is different from the monomer. Each of the monomer and the at

least one comonomer that is different from the monomer may be selected from any of the suitable monomers discussed previously.

[0053] In further embodiments, L^1 is a copolymer comprising units derived from two different types of monomers, such as a monomer and a comonomer. Accordingly, in certain embodiments, L^1 is a copolymer comprising units derived from a monomer and a comonomer that is different from the monomer. Each of the monomer and the comonomer may be selected from any of the suitable monomers discussed previously.

[0054] In certain embodiments, L^1 is an ethylene/alpha-olefin copolymer. In some embodiments, L^1 is an ethylene/alpha-olefin copolymer comprising units derived from ethylene and a C_3 to C_{30} alpha-olefin, wherein each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$ comprises an amount of ethylene that is greater than or equal to 50 wt%, or greater than or equal to 60 wt%, or greater than or equal to 70 wt%, or greater than or equal to 75 wt%, or greater than or equal to 80 wt%, or greater than or equal to 85 wt%, or greater than or equal to 88 wt%, or greater than or equal to 89 wt%, or greater than or equal to 90 wt%, based on the total weight of each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$. The C_3 to C_{30} alpha-olefin may be selected from any of the suitable alpha-olefins discussed previously. In certain embodiments, the C_3 to C_{30} alpha-olefin may be propylene, isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, or the like. In some embodiments, L^1 is an ethylene/alpha-olefin copolymer comprising units derived from ethylene and a C_3 to C_{30} alpha-olefin, wherein the C_3 to C_{30} alpha-olefin is selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene.

[0055] In further embodiments, L^1 is a propylene/alpha-olefin copolymer. L^1 may be a propylene/alpha-olefin copolymer comprising units derived from propylene and either ethylene or a C_4 to C_{30} alpha-olefin, wherein each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$ comprises an amount of propylene that is greater than or equal to 50 wt%, or greater than or equal to 60 wt%, or greater than or equal to 70 wt%, or greater than or equal to 75 wt%, or greater than or equal to 80 wt%, or greater than or equal to 85 wt%, or greater than or equal to 88 wt%, or greater than or equal to 89 wt%, or greater than or equal to 90 wt%, based on the total weight of each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$. The C_4 to C_{30} alpha-olefin may be any of the suitable alpha-olefins discussed above. In certain embodiments, the C_4 to C_{30} alpha-olefin may be isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, or the like. In certain

embodiments, L^1 may be a propylene/alpha-olefin copolymer comprising units derived from propylene and either ethylene or a C_4 to C_{30} alpha-olefin, wherein the C_4 to C_{30} alpha-olefin is selected from the group consisting of 1-butene, 1-hexene, and 1-octene.

[0056] In certain embodiments, L^1 is a terpolymer comprising units derived from three different types of monomers, each of which may be selected from any of the suitable monomers discussed above. In further embodiments, L^1 is a terpolymer comprising ethylene or propylene as a first monomer, a C_3 to C_{30} alpha-olefin or styrene as a second monomer, and a diene or polar monomer as a third monomer.

[0057] In some embodiments, L^1 comprises from 0 to 10 wt% of units derived from diene monomers. For example, L^1 may comprise from 1 to 8 wt%, or from 1 to 5 wt%, or from 1 to 3 wt% of units derived from diene monomers. In further embodiments, L^1 may be substantially free of units derived from diene monomers. For example, in certain embodiments, L^1 may comprise from 0 to 0.2 wt%, or from 0 to 0.01 wt%, or from 0 to 0.001 wt%, or from 0 to 0.0001 wt% of units derived from diene monomers.

[0058] In certain embodiments, L^1 is an olefin block copolymer as defined herein. In further embodiments, L^1 is a block composite, a specified block composite, or a crystalline block composite as defined herein.

[0059] In certain embodiments, L^2 is $–CH_2CH(Y^2)–$, such that the telechelic polyolefin is $A^1L^1CH_2CH(Y^2)A^2$, wherein Y^2 is hydrogen or a C_1 to C_{30} hydrocarbyl group. In certain embodiments, the Y^2 group is hydrogen. In further embodiments, the Y^2 group is a C_1 to C_{10} alkyl group, or a C_1 to C_6 alkyl group, or a C_1 to C_3 alkyl group. In further embodiments, the Y^2 group is an ethyl group.

[0060] In some embodiments, A^2 is a hydrocarbyl group comprising a hindered double bond. In further embodiments, A^2 is a hydrocarbyl group comprising two or more hindered double bonds.

[0061] In certain embodiments, due to the hindered double bond, the A^2 group is a group that is not readily incorporated by an active catalyst under the process conditions used to make the polyolefin L^1, such that direct incorporation of A^2 along the backbone chain of L^1 is less than or equal to 0.5 mol%, or less than or equal to 0.1 mol%, or is not detected, as determined by the ^{13}C NMR method described herein or similar ^{13}C NMR methods.

[0062] In some embodiments, A^2 is a hydrocarbyl group comprising a hindered double bond, wherein the hindered double bond is selected from the group consisting of the double bond of

a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.

[0063] In further embodiments, A^2 is a hydrocarbyl group comprising two or more hindered double bonds, wherein each hindered double bond is independently selected from the group consisting of the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.

[0064] In certain embodiments, A^2 is a hydrocarbyl group comprising a functional group, wherein the functional group is selected from the group consisting of a vinylidene group, a vinylene group, a trisubstituted alkene, and a vinyl group attached to a branched alpha carbon.

[0065] In further embodiments, A^2 is a hydrocarbyl group comprising two or more functional groups, wherein each functional group is independently selected from the group consisting of a vinylidene group, a vinylene group, a trisubstituted alkene, and a vinyl group attached to a branched alpha carbon.

[0066] The A^2 group may be a cyclic or acyclic (linear or branched) hydrocarbyl group. If A^2 is a cyclic hydrocarbyl group, A^2 may comprise one or more rings, wherein each ring may be a monocyclic, bicyclic, or polycyclic ring, and wherein each ring may comprise one or more hindered double bonds.

[0067] Furthermore, if A^2 is a cyclic hydrocarbyl group, each hindered double bond or functional group therein may be an endocyclic double bond, an exocyclic double bond, or an acyclic double bond. For example, A^2 may be a cyclic hydrocarbyl group comprising a vinylene group, wherein the double bond of the vinylene group may be an endocyclic double bond or an acyclic double bond. In further embodiments, A^2 may be a cyclic hydrocarbyl group comprising a vinylidene group, wherein the double bond of the vinylidene group may be an exocyclic double bond or an acyclic double bond. In further embodiments, A^2 may be a cyclic hydrocarbyl group comprising a trisubstituted alkene, wherein the double bond of the trisubstituted alkene may be an endocyclic double bond, an exocyclic double bond, or an acyclic double bond. In further embodiments, A^2 may be a cyclic hydrocarbyl group comprising a vinyl group attached to a branched alpha carbon, wherein the vinyl group attached to a branched alpha carbon is an acyclic double bond.

[0068] In any of the embodiments described herein, A^2 may comprise from 3 to 30 carbon atoms, or from 3 to 25 carbon atoms, or from 3 to 20 carbon atoms, or from 3 to 15 carbon

atoms, or from 3 to 10 carbon atoms, or from 3 to 9 carbon atoms, or from 3 to 8 carbon atoms, or from 3 to 7 carbon atoms, or from 3 to 6 carbon atoms, or from 3 to 5 carbon atoms, or from 3 to 4 carbon atoms, or 3 carbon atoms.

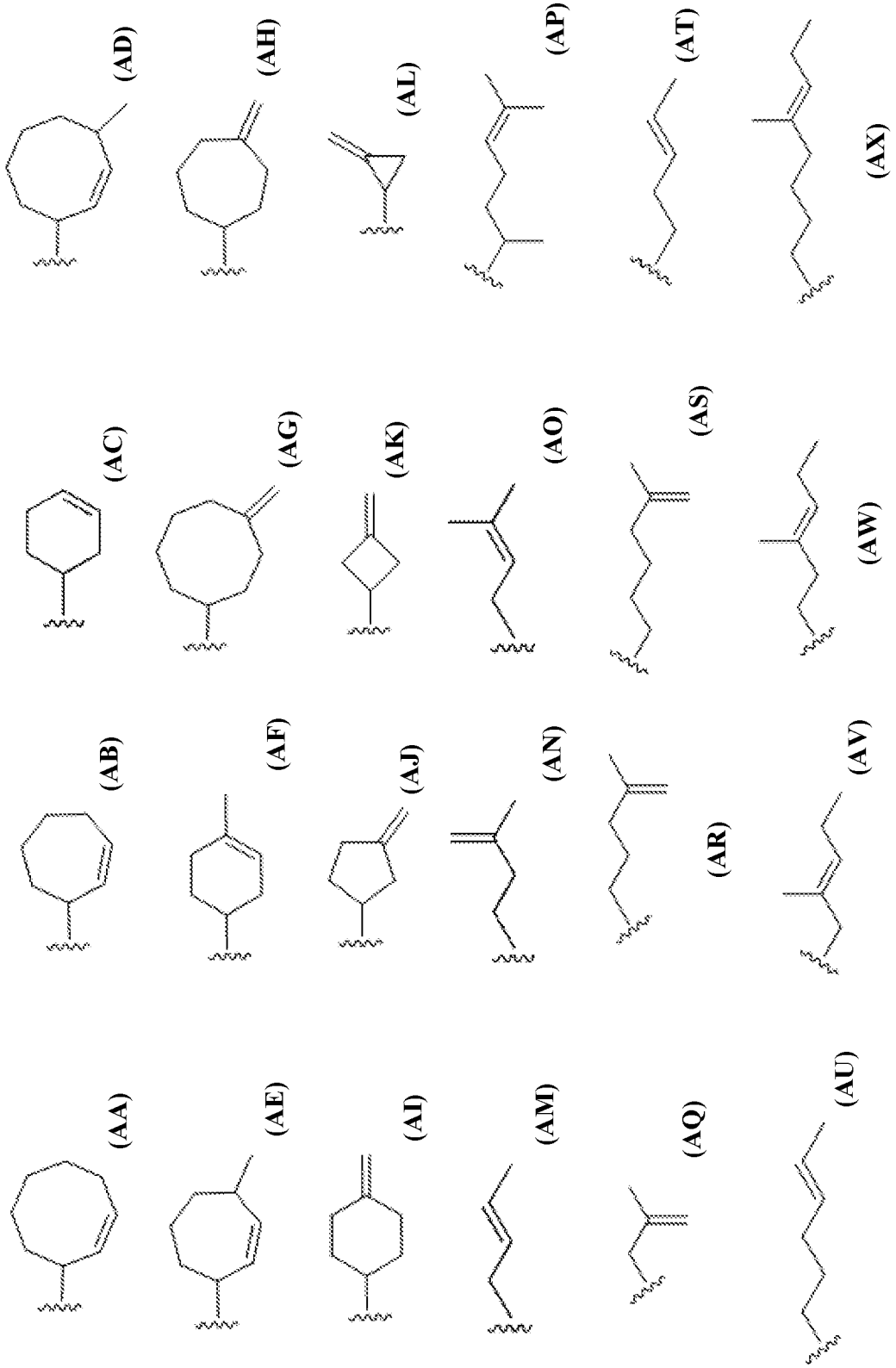
[0069] In certain embodiments, A^2 is a C_3 to C_{30} cyclic hydrocarbyl group comprising an alkyl-substituted or unsubstituted cycloalkene. In further embodiments, A^2 is an alkyl-substituted or unsubstituted cycloalkene comprising from 3 to 30 carbon atoms, or from 3 to 25 carbon atoms, or from 3 to 20 carbon atoms, or from 3 to 15 carbon atoms, or from 3 to 10 carbon atoms, or from 3 to 9 carbon atoms, or from 3 to 8 carbon atoms, or from 3 to 7 carbon atoms, or from 3 to 6 carbon atoms.

[0070] Exemplary unsubstituted cycloalkenes include but are not limited to cyclohexene, cycloheptene, cyclooctene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1,5-cyclooctadiene. Exemplary alkyl-substituted cycloalkenes include but are not limited to alkyl-substituted cyclohexene, alkyl-substituted cycloheptene, alkyl-substituted cyclooctene, alkyl-substituted 1,3-cyclohexadiene, alkyl-substituted 1,4-cyclohexadiene, and alkyl-substituted1,5-cyclooctadiene.

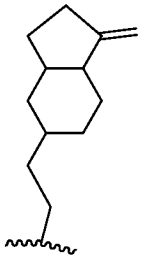
[0071] In some embodiments, A^2 is a methyl-substituted or unsubstituted cycloalkene selected from the group consisting of a methyl-substituted or unsubstituted cyclohexene, a methyl-substituted or unsubstituted cycloheptene, and a methyl-substituted or unsubstituted cyclooctene. In some embodiments, A^2 is a methyl-substituted or unsubstituted cyclohexene.

[0072] In some embodiments, A^2 is a C_1 to C_{10} acyclic alkyl group, or a C_3 to C_{10} acyclic alkyl group, or a C_4 to C_8 acyclic alkyl group.

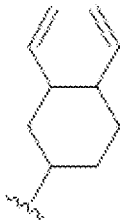
[0073] Exemplary A^2 groups include but are not limited to the following:


(AA)
(AB)
(AC)
(AD)
(AE)
(AF)
(AG)
(AH)
(AI)
(AJ)
(AK)
(AL)
(AM)
(AN)
(AO)
(AP)
(AQ)
(AR)
(AS)
(AT)
(AU)
(AV)
(AW)
(AX)

(AZ1)



(AZ)



(AY)



[0074] With regard to each of (AA) to (AZ) and (AZ1), the ~~~ symbol (squiggly line symbol) denotes the point of connection to L^2 in the formula $A^1L^1L^2A^2$, for example, the point of connection to the carbon attached to a hydrogen, "Y^2," and "$A^1L^1CH_2$" in the formula $A^1L^1CH_2CH(Y^2)A^2$. In addition, with regard to each of (AA) to (AZ) and (AZ1), the ~~~ symbol (squiggly line symbol) denotes the point of connection to the carbon attached to a hydrogen and Y^2 in the chain transfer agent formulas of $Al(CH_2CH(Y^2)A^2)_3$ and $Zn(CH_2CH(Y^2)A^2)_2$ discussed below.

[0075] With regard to each of (AA) to (AF), the endocyclic double bond may be between any two adjacent carbon atoms that are ring members.

[0076] With regard to each of (AD) to (AF), the pendant methyl group may be connected to any carbon atom that is a ring member.

[0077] With regard to each of (AG) to (AL), the exocyclic double bond may be connected to any ring member carbon atom that is not already connected to more than two carbon atoms.

[0078] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the GPC method described herein or similar GPC methods, a weight average molecular weight (Mw) of from 1,000 to 40,000 g/mol, or from 1,000 to 35,000 g/mol, or from 1,000 to 30,000 g/mol, or from 1,000 to 25,000 g/mol.

[0079] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the GPC method described herein or similar GPC methods, a number average molecular weight (Mn) of from 1,000 to 18,000 g/mol, or from 1,000 to 16,000 g/mol, or from 1,000 to 14,000 g/mol, or from 1,000 to 12,000 g/mol, or from 1,000 to 10,000 g/mol.

[0080] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the GPC method described herein or similar GPC methods, an average molar mass (Mz) of from 1,000 to 125,000 g/mol, or from 1,000 to 100,000 g/mol, or from 1,000 to 75,000 g/mol, or from 1,000 to 60,000 g/mol, or from 10,000 to 50,000 g/mol.

[0081] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the GPC method described

herein or similar GPC methods, a Mw/Mn (PDI) of from 1 to 10, or from 1 to 7, or from 1 to 5, or from 1.5 to 4, or from 2 to 4.

[0082] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with ASTM D-792, Method B, a density of from 0.850 to 0.965 g/cc, or from 0.854 to 0.950 g/cc, or from 0.854 to 0.935 g/cc, or from 0.854 to 0.925 g/cc, or from 0.854 to 0.910 g/cc, or from 0.854 to 0.900 g/cc, or from 0.854 to 0.885 g/cc, or from 0.854 to 0.880 g/cc, or from 0.854 to 0.875 g/cc.

[0083] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with ASTM D-1238, condition 190°C/2.16 kg, a melt index (I2) of from 50 to 2000 g/10 minutes, or from 100 to 2,000 g/10 minutes, or from 200 to 1,500 g/10 minutes, or from 300 to 1,200 g/10 minutes, or from 400 to 1,100 g/10 minutes.

[0084] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the DSC method described herein or similar DSC methods, a T_m in the range of from -25 °C to 165 °C, or from -25 °C to 150 °C, or from -25 °C to 125 °C, or from -25 °C to 100 °C, or from 0 °C to 80 °C, or from 10 °C to 60 °C.

[0085] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with ASTM D-3236, a Brookfield viscosity (as measured at 177 °C) of from 10 to 100,000 cP, or from 50 to 100,000 cP, or from 500 to 100,000 cP, or from 1,000 to 50,000 cP, or from 1,000 to 40,000 cP, or from 5,000 to 15,000 cP.

[0086] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the DSC method described herein or similar DSC methods, an enthalpy of melting (ΔHm) of from 0 to 235 J/g, or from 0 to 200 J/g, or from 10 to 175 J/g, or from 10 to 150 J/g, or from 10 to 125 J/g, or from 20 to 117 J/g.

[0087] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the DSC method described herein or similar DSC methods, a wt% crystallinity of from 0 to 80%, or from 0 to 60%, or from 5 to 50%, or from 7 to 40%, based on PE ΔHm of 292 J/g.

[0088] In some embodiments, the (A) polyolefin component (or each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$) comprises or has, in accordance with the DSC method described herein or similar DSC methods, a T_g of from -80 to 100 °C, or from -80 to 75 °C, or from -80 to 50 °C, or from -80 to 25 °C, or from -80 to 0 °C, or from -80 to -15 °C, or from -70 to -30 °C.

[0089] In some embodiments, L^1 is substantially free of units derived from diene monomers, and the polyolefin of the formula A^1L^1 comprises a total number of unsaturations of equal to or greater than 0.6, or equal to or greater than 0.7, or equal to or greater than 0.8, or equal to or greater than 0.9, or equal to or greater than 1.0, or equal to or greater than 1.1, or equal to or greater than 1.2, or equal to or greater than 1.3; and the polyolefin of the formula $A^1L^1L^2A^2$ comprises a total number of unsaturations of equal to or greater than 1.1, or equal to or greater than 1.2, or equal to or greater than 1.3, or equal to or greater than 1.4, or equal to or greater than 1.5, or equal to or greater than 1.6, or equal to or greater than 1.7, or equal to or greater than 1.8, or equal to or greater than 1.9 The total number of unsaturations may be defined as (unsaturations/1000C)*(1000C/chain) = (unsaturations/1000C)*(Mn/M_{CH2}/1000), where unsaturations/1000C is measured by ^{1}H NMR, Mn is the number average molecular weight as measured by GPC and corrected for composition as measured by ^{13}C NMR, M_{CH2} = 14 g/mol. As reported, Mn measured by GPC is the polymer backbone number average molecular weight. Unsaturations/1000C as measured by 1H NMR is relative to total carbons in the polymer chain. For ethylene, propylene, octene, and ethylidene norbornene there are 2, 3, 8, and 9 total carbon atoms respecitively, per 2 backbone carbon atoms. Therefore, the Mn corrected for composition is Mn as measured by GPC times (mol% C2/2 + mol% C3/3 + mol% C8/8 + mol% ENB/9)/2. ^{13}C NMR, ^{1}H NMR, and GPC here refer to the methods described herein or similar methods. "Substantially free," as used here, refers to, for example, L^1 comprising from 0 to 0.001 wt% of units derived from diene monomers, based on the total weight of each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$.

[0090] In some embodiments, L^1 comprises from 1 to 8 wt%, or from 1 to 5 wt%, or from 1 to 3 wt% of units derived from diene monomers, based on the total weight of each of the polyolefins of the formulas A^1L^1 and $A^1L^1L^2A^2$, and the polyolefin of the formula A^1L^1 comprises a total number of unsaturations of equal to or greater than (X^D+0.6), equal to or greater than (X^D+0.7), equal to or greater than (X^D+0.8), equal to or greater than (X^D+0.9), equal to or greater than (X^D+1), equal to or greater than (X^D+1.1), equal to or greater than (X^D+1.2), or equal to or

greater than (X^D+1.3), and the polyolefin of the formula $A^1L^1L^2A^2$ comprises a total number of unsaturations of equal to or greater than (X^D+1.1), equal to or greater than (X^D+1.2), equal to or greater than (X^D+1.3), equal to or greater than (X^D+1.4), equal to or greater than (X^D+1.5), equal to or greater than (X^D+1.6), equal to or greater than (X^D+1.7), equal to or greater than (X^D+1.8), or equal to or greater than (X^D+1.9), wherein X^D is the number of unsaturations from the units derived from diene monomers in L^1, and wherein unsaturations are measured as described in the previous paragraph.

Preparing the (A) Polyolefin Component

[0091] The present disclosure further relates to a process for preparing a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1, the process comprising:

1) combining starting materials comprising (a1) a monomer component, (b1) a chain transfer agent component, and (c1) a catalyst component comprising a procatalyst to form a solution and polymerizing from greater than 10 mol% to less than or equal to 99 mol% of the (a1) monomer component in the solution;

2) heating the solution; and

3) recovering a product comprising the polyolefin component comprising the unsaturated polyolefin of the formula A^1L^1, wherein:

the (b1) chain transfer agent component comprises an aluminum alkyl of the formula $Al(d)_3$, and

d at each occurrence independently is a C_1 to C_{10} alkyl group;

L^1 is a polyolefin;

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

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

[0092] The present disclosure further relates to a process for preparing a polyolefin component comprising a telechelic polyolefin of the formula $A^1L^1L^2A^2$, the process comprising:

1) combining starting materials comprising (a1) a monomer component, (b1) a chain transfer agent component, and (c1) a catalyst component comprising a procatalyst to form a solution and polymerizing from greater than 10 mol% to less than or equal to 99 mol% of the (a1) monomer component in the solution;

2) heating the solution; and

3) recovering a product comprising the polyolefin component comprising the telechelic polyolefin of the formula $A^1L^1L^2A^2$, wherein:

the (b1) chain transfer agent component comprises an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$;

L^1 at each occurrence independently is a polyolefin;

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

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

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

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

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

[0093] The present disclosure further relates to a process for preparing a polyolefin component comprising a polyolefin of the formula A^1L^1 and a telechelic polyolefin of the formula $A^1L^1L^2A^2$, the process comprising:

1) combining starting materials comprising (a1) a monomer component, (b1) a chain transfer agent component, and (c1) a catalyst component comprising a procatalyst to form a solution and polymerizing from greater than 10 mol% to less than or equal to 99 mol% of the (a1) monomer component in the solution;

2) heating the solution; and

3) recovering a product comprising the polyolefin component comprising the polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$, wherein:

the (b1) chain transfer agent component comprises an aluminum alkyl of the formula $Al(d)_3$ and an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$;

d at each occurrence independently is a C_1 to C_{10} alkyl group;

L^1 at each occurrence independently is a polyolefin;

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

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

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

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

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

[0094] Each of the high flow unsaturated polyolefin of the formula A^1L^1 and the high flow telechelic polyolefin of the formula $A^1L^1L^2A^2$ prepared by the above processes may comprise a weight average molecular weight from 1,000 to 40,000 g/mol. Polymers other than the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ that are suitable as the component (D) polymer (discussed below) may be prepared independently from the above processes and subsequently blended with the unsaturated polyolefin of the formula A^1L^1 and/or the telechelic polyolefin of the formula $A^1L^1L^2A^2$.

[0095] For the process of preparing a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1 and a telechelic polyolefin of the formula $A^1L^1L^2A^2$, the (b1) chain transfer agent component may comprise a ratio of the aluminum alkyl of the formula $Al(d)_3$ to the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ from 1:99 to 99:1, or from 10:90 to 90:10, or from 20:80 to 80:20, or from 30:70 to 70:30, or from 40:60 to 60:40, or 50:50

[0096] The previously described embodiments for each of the L^1, A^1, Y^1, L^2, Y^2, and A^2 groups apply with respect to the present processes disclosed herein. Similarly, the previously described embodiments for the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ apply with respect to the present processes disclosed herein.

[0097] The starting materials in step 1) of any of the above processes may further comprise a (d1) solvent. The (d1) solvent of the starting materials may be any aromatic or aliphatic hydrocarbon. Suitable solvents include but are not limited to toluene, xylene, hexane, pentane, benzene, heptane, Isopar^{TM}, and combinations thereof. Beyond this, the starting materials in step 1) may further comprise hydrogen, adjuvants, scavengers, and/or polymerization aids.

[0098] Step 1) of any of the above processes is a coordination polymerization step to form L^1 from the monomers and comonomers of the (a1) monomer component. During step 1), polymeryl aluminum species can form via chain transfer between the (b1) chain transfer agent component and an active catalyst from the (c1) catalyst component. Subsequently, the polymeryl aluminum species undergo beta-hydride elimination during step 2) to form a product comprising the unsaturated polyolefin of the formula A^1L^1 and/or the telechelic polyolefin of the formula $A^1L^1L^2A^2$ of the (A) polyolefin component, which is recovered during step 3).

[0099] Step 1) of any of the above processes preferably carried out as a solution polymerization step. Most preferably, step 1) is performed as a continuous solution polymerization step in which the starting materials are continuously supplied to a reaction zone and polymer products are continuously removed therefrom. Within the scope of the terms "continuous" and "continuously," as used in this context, are those processes in which there are intermittent additions of reactants and removal of products at regular or irregular intervals, so that, over time, the overall process is substantially continuous.

[0100] Step 1) of any of the above processes may be performed at a temperature from 60°C, or 80°C, or 100°C, or 110°C, or 115°C to 120°C, or 130°C, or 140°C, or 150°C. For example, in certain embodiments, step 1) may be performed at a temperature from 60 to 150°C, or from 80 to 140°C, or from 100 to 130°C.

[0101] One of ordinary skill in the art would understand that the amounts of each component of the starting materials, including components (a1) to (d1), may be varied in order to produce polymers differing in one or more chemical or physical properties.

[0102] Without limiting in any way the scope of the invention, one means for carrying out step 1) is as follows. In a stirred-tank reactor, the monomers of the (a1) monomer component are introduced continuously together with any solvent or diluent. The reactor contains a liquid phase composed substantially of monomers together with any solvent or diluent and dissolved polymer. Preferred solvents include C_{4-10} 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. The (b1) chain transfer agent component and the (c1) catalyst component are continuously or intermittently introduced in the reactor liquid phase or any recycled portion thereof. The reactor temperature and pressure may be controlled by adjusting the solvent/monomer ratio, the addition rate of the (c1) catalyst component, as well as by cooling or heating coils, jackets or both. The polymerization rate is controlled by the rate of addition of the (c1) catalyst component. If the (a1) monomer component comprises ethylene and at least one comonomer, the ethylene content of the polymer product is determined by the ratio of ethylene to comonomer 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 others known in the art. In a continuous process, the mean residence time of the active catalyst and polymer in the reactor generally is from 5 minutes to 8 hours, and preferably from 10 minutes to 6 hours.

[0103] Alternatively, step 1) of any of the above processes may be conducted under differentiated process conditions in two or more reactors, connected in series, operating under steady state polymerization conditions or in two or more zones of a reactor operating under plug flow polymerization conditions. Alternatively, step 1) of any of the above processes may be conducted in one or more continuous loop reactors with or without monomer, catalyst, or chain transfer agent gradients established between differing regions thereof, optionally accompanied by separated addition of catalysts and/or chain transfer agent, and operating under adiabatic or non-adiabatic solution polymerization conditions or combinations of the foregoing reactor conditions.

[0104] Following step 1), the polymer solution is heated in accordance with step 2), as further described below. Such heating includes, but is not limited to, heating in a post-reactor heater. Following step 2), the polymer product is recovered in step 3) by means known in the art. Such

means include contacting the polymer solution with a catalyst kill agent such as water, steam or an alcohol, flashing off gaseous monomers as well as residual solvent or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder.

[0105] In some embodiments, the solution in step 2) of any of the above processes is heated at a temperature of at least 160°C, or at least 180°C, or at least 200°C, or at least 210°C, or at least 220°C, or at least 230°C, or at least 240°C, or at least 250°C, or at least 260°C, or at least 270°C, or at least 280°C, or at least 290°C, or at least 300°C.

[0106] In some embodiments, the solution in step 2) of any of the above processes is heated at a temperature of at least 160°C, or at least 180°C, or at least 200°C, or at least 210°C, or at least 220°C, or at least 230°C, or at least 240°C, or at least 250°C, or at least 260°C, or at least 270°C, or at least 280°C, or at least 290°C, or at least 300°C for a time of at least 30 seconds, or at least 1 minute, or at least 5 minutes, or at least 10 minutes, or at least 15 minutes, or at least 20 minutes, or at least 30 minutes, or at least 45 minutes, or at least 1 hour, or at least 6 hours, or least 12 hours, or at least 18 hours, or at least 24 hours

[0107] In some embodiments, the solution in step 2) of any of the above processes is heated to a temperature of at least 160°C, or at least 180°C, or at least 200°C, or at least 210°C, or at least 220°C, or at least 230°C, or at least 240°C, or at least 250°C, or at least 260°C, or at least 270°C, or at least 280°C, or at least 290°C, or at least 300°C and held at a temperature of at least 160°C, or at least 180°C, or at least 200°C, or at least 210°C, or at least 220°C, or at least 230°C, or at least 240°C, or at least 250°C, or at least 260°C, or at least 270°C, or at least 280°C, or at least 290°C, or at least 300°C for a time of at least 30 seconds, or at least 1 minute, or at least 5 minutes, or at least 10 minutes, or at least 15 minutes, or at least 20 minutes, or at least 30 minutes, or at least 45 minutes, or at least 1 hour, or at least 6 hours, or least 12 hours, or at least 18 hours, or at least 24 hours.

[0108] For example, in certain embodiments, the solution in step 2) of any of the above processes is heated at a temperature from 160 to 300°C, or from 180 to 300°C, or from 200 to 300°C, or from 210 to 300°C, or from 220 to 290°C, or from 230 to 290°C, or from 240 to 280°C.

[0109] In further embodiments, the solution in step 2) of any of the above processes is heated at a temperature from 160 to 300°C, or from 180 to 300°C, or from 200 to 300°C, or from 210 to

300°C, or from 220 to 290°C, or from 230 to 290°C, or from 240 to 280°C for a time from 30 seconds to 24 hours, or from 30 seconds to 18 hours, or from 30 seconds to 12 hours, or from 30 seconds to 6 hours, or from 30 seconds to 1 hour, or from 30 seconds to 45 minutes, or from 30 seconds to 30 minutes, or from 30 seconds to 20 minutes, or from 1 minute to 20 minutes, or from 5 minutes to 20 minutes.

[0110] In further embodiments, the solution in step 2) of any of the above processes is heated to a temperature from 160 to 300°C, or from 180 to 300°C, or from 200 to 300°C, or from 210 to 300°C, or from 220 to 290°C, or from 230 to 290°C, or from 240 to 280°C and held at a temperature from 160 to 300°C, or from 180 to 300°C, or from 200 to 300°C, or from 210 to 300°C, or from 220 to 290°C, or from 230 to 290°C, or from 240 to 280°C for a time from 30 seconds to 24 hours, or from 30 seconds to 18 hours, or from 30 seconds to 12 hours, or from 30 seconds to 6 hours, or from 30 seconds to 1 hour, or from 30 seconds to 45 minutes, or from 30 seconds to 30 minutes, or from 30 seconds to 20 minutes, or from 1 minute to 20 minutes, or from 5 minutes to 20 minutes.

The (a1) monomer component

[0111] The (a1) monomer component comprises any monomer selected from the monomers and comonomers discussed herein with regard to L^1. Examples of suitable monomers and comonomers include but are not limited to ethylene and alpha-olefins of 3 to 30 carbon atoms, preferably 3 to 20 carbon atoms, such as propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 5-ethyl-1-nonene, 1-octadecene and 1-eicosene; conjugated or nonconjugated dienes, such as butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,5-heptadiene, 1,6-heptadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, 1,9-decadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene, 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene, and mixed isomers of dihydromyrcene and dihydroocimene; norbornene and alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, 5-methylene-2-norbornene, 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, and norbornadiene; aromatic vinyl compounds such as styrenes, mono or poly

alkylstyrenes (including styrene, o-methylstyrene, t-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene and p-ethylstyrene).

[0112] In some embodiments, the (a1) monomer component comprises ethylene monomers. In some embodiments, the (a1) monomer component comprises propylene monomers. In some embodiments, the (a1) monomer component comprises ethylene monomers and comonomers of a C3 to C30 alpha-olefin. The C3 to C30 alpha olefin may be selected from propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 5-ethyl-1-nonene, 1-octadecene and 1-eicosene. In some embodiments, the (a1) monomer component comprises propylene monomers and comonomers of ethylene or a C4 to C30 alpha-olefin. The C4 to C30 alpha-olefin may be selected from 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 5-ethyl-1-nonene, 1-octadecene and 1-eicosene.

[0113] In certain embodiments, the (a1) monomer component comprises ethylene monomers and comonomers of a C3 to C30 alpha-olefin, wherein the C3 to C30 alpha-olefin is selected from the group consisting of propylene, 1-hexene, 1-butene, and 1-octene. In further embodiments, the (a1) monomer component comprises ethylene monomers and propylene comonomers. In further embodiments, the (a1) monomer component comprises ethylene monomers and 1-hexene comonomers. In further embodiments, the (a1) monomer component comprises ethylene monomers and 1-butene comonomers. In further embodiments, the (a1) monomer component comprises ethylene monomers and 1-octene comonomers.

[0114] In further embodiments, the (a1) monomer component comprises propylene monomers and comonomers of ethylene or a C4 to C30 alpha-olefin, wherein the C4 to C30 alpha-olefin is selected from the group consisting of 1-hexene, 1-butene, and 1-octene. In further embodiments, the (a1) monomer component comprises propylene monomers and ethylene comonomers. In further embodiments, the (a1) monomer component comprises propylene monomers and 1-hexene comonomers. In further embodiments, the (a1) monomer component comprises propylene monomers and 1-butene comonomers. In further embodiments, the (a1) monomer component comprises propylene monomers and 1-octene comonomers.

[0115] In certain embodiments, the (a1) monomer component comprises from greater than or equal to 50 wt% to less than or equal to 99 wt% (e.g., from greater than or equal to 60 wt% to

less than or equal to 99 wt%, or from greater than or equal to 70 wt% to less than or equal to 99 wt%, or from greater than or equal to 75 wt% to less than or equal to 99 wt%, or from greater than or equal to 80 wt% to less than or equal to 99 wt%, or from greater than or equal to 85 wt% to less than or equal to 99 wt%, or from greater than or equal to 90 wt% to less than or equal to 99 wt%) of ethylene monomers and from greater than or equal to 1 wt% to less than or equal to 50 wt% (e.g., from greater than or equal to 1 wt% to less than or equal to 40 wt%, or from greater than or equal to 1 wt% to less than or equal to 30 wt%, or from greater than or equal to 1wt% to less than or equal to 25 wt%, or from greater than or equal to 1 wt% to less than or equal to 20 wt%, or from greater than or equal to 1 wt% to less than or equal to 15 wt%, or from greater than or equal to 1 wt% to less than or equal to 10 wt%) of comonomers of a C3 to C30 alpha-olefin, wherein the C3 to C30 alpha-olefin is selected from the group consisting of propylene, 1-hexene, 1-butene, and 1-octene.

[0116] In certain embodiments, the (a1) monomer component comprises from greater than or equal to 50 wt% to less than or equal to 99 wt% (e.g., from greater than or equal to 60 wt% to less than or equal to 99 wt%, or from greater than or equal to 70 wt% to less than or equal to 99 wt%, or from greater than or equal to 75 wt% to less than or equal to 99 wt%, or from greater than or equal to 80 wt% to less than or equal to 99 wt%, or from greater than or equal to 85 wt% to less than or equal to 99 wt%, or from greater than or equal to 90 wt% to less than or equal to 99 wt%) of propylene monomers and from greater than or equal to 1 wt% to less than or equal to 50 wt% (e.g., from greater than or equal to 1 wt% to less than or equal to 40 wt%, or from greater than or equal to 1 wt% to less than or equal to 30 wt%, or from greater than or equal to 1wt% to less than or equal to 25 wt%, or from greater than or equal to 1 wt% to less than or equal to 20 wt%, or from greater than or equal to 1 wt% to less than or equal to 15 wt%, or from greater than or equal to 1 wt% to less than or equal to 10 wt%) of comonomers of ethylene or a C4 to C30 alpha-olefin, wherein the C4 to C30 alpha-olefin is selected from the group consisting of 1-hexene, 1-butene, and 1-octene.

[0117] In some embodiments, the (a1) monomer component comprises from 0 to 10 wt% of diene monomers. For example, the (a1) monomer component may comprise from 0.5 to 8 wt%, or from 1 to 5 wt%, or from 1 to 3 wt% of diene monomers. In further embodiments, the (a1) monomer component may be substantially free of diene monomers. For example, in certain

embodiments, the (a1) monomer component may comprise from 0 to 0.2 wt%, or from 0 to 0.01 wt%, or from 0 to 0.001 wt%, or from 0 to 0.0001 wt% of diene monomers.

The (b1) chain transfer agent component

[0118] The (b1) chain transfer agent component may comprise any chain transfer agent described herein or disclosed in U.S. provisional application nos. 62/786084, 62/786100, 62/786119, and 62/786110.

[0119] The aluminum alkyl of the formula $Al(d)_3$ may be a tri(C_{1-8}) alkyl aluminum. Non-limiting examples of the aluminum alkyl of the formula $Al(d)_3$ are triethyl aluminum, tri(i-propyl) aluminum, tri(i-butyl) aluminum, tri(n-hexyl) aluminum, and tri(n-octyl) aluminum.

[0120] Without being bound by any particular theory, the aluminum alkyl of the formula $Al(d)_3$ contributes to the formation of the unsaturated polyolefin of the formula A^1L^1 while organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ contributes to the formation of the telechelic polyolefin of the formula $A^1L^1L^2A^2$.

[0121] In certain embodiments, the (b1) chain transfer agent component comprises an organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$, wherein: Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond. In further embodiments, the (b1) chain transfer agent component is the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$. Y^2 and A^2 may be any of the previously described embodiments. In certain embodiments, Y^2 of the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ may be selected from the group consisting of hydrogen, a methyl group, and an ethyl group. In certain embodiments, A^2 of the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 of the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ is selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

[0122] The organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ may be prepared by a thermal process comprising: (a) combining starting materials comprising a hydrocarbon of the formula $CH_2=C(Y^2)A^2$, an aluminum alkyl of the formula $Al(d)_3$, and an optional solvent to form an organoaluminum solution, (b) heating the organoaluminum solution to a temperature from 60

to 200°C, or from 80 to 180°C, or from 100 to 150°C, or from 110 to 130°C and holding the organo-aluminum solution at the temperature of from 60 to 200°C, or from 80 to 180°C, or from 100 to 150°C, or from 110 to 130°C for a time from 30 minutes to 200 hours, or from 30 minutes to 100 hours, or from 30 minutes to 50 hours, or from 30 minutes to 25 hours, or from 1 hour to 10 hours, or from 1 hour to 5 hours, or from 3 hours to 5 hours, and (c) recovering a product comprising the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$, wherein: d at each occurrence independently is a C_1 to C_{10} alkyl group; Y^2 at each occurrence independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond. In certain embodiments, the carbon of d that is attached to Al is a carbon that is connected to a tertiary carbon. For example, in certain embodiments, the aluminum alkyl of the formula $Al(d)_3$ is triisobutylaluminum. In certain embodiments, in step (b), the organoaluminum solution is heated at a temperature from 60 to 200°C, or from 80 to 180°C, or from 100 to 150°C, or from 110 to 130°C. In further embodiments, in step (b), the organoaluminum solution is heated at a temperature from 60 to 200°C, or from 80 to 180°C, or from 100 to 150°C, or from 110 to 130°C for a time from 30 minutes to 200 hours, or from 30 minutes to 100 hours, or from 30 minutes to 50 hours, or from 30 minutes to 25 hours, or from 1 hour to 10 hours, or from 1 hour to 5 hours, or from 3 hours to 5 hours.

[0123] For the thermal process of preparing the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$, Y^2 and A^2 may be any of the previously described embodiments. The optional solvent may be any discussed herein. The starting materials in step (a) may comprise a ratio of the aluminum alkyl of the formula $Al(d)_3$ to the hydrocarbon of the formula $CH_2=C(Y^2)A^2$ of 1:10, or 1:5, or 1:3. The starting materials in step (a) may comprise one or more hydrocarbons of the formula $CH_2=C(Y^2)A^2$, wherein: Y^2 at each occurrence of each hydrocarbon independently is hydrogen or a C_1 to C_{30} hydrocarbyl group; A^2 at each of occurrence of each hydrocarbon independently is a hydrocarbyl group comprising a hindered double bond; and the starting materials comprise a ratio of the aluminum alkyl of the formula $Al(d)_3$ to the one or more hydrocarbons of the formula $CH_2=C(Y^2)A^2$ of 1:10, or 1:5, or 1:3. In certain embodiments, Y^2 may be selected from the group consisting of hydrogen, a methyl group, and an ethyl group, and A^2 may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 may be selected from the group consisting of

(AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member. In this process of preparing the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$, any excess hydrocarbon of the formula $CH_2=C(Y^2)A^2$ may be removed through the use of vacuum and optional heating.

[0124] Alternatively, the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$ may be prepared a catalytic process comprising: (a) combining starting materials comprising a hydrocarbon of the formula $CH_2=CHA^2$, an aluminum alkyl of the formula $Al(Y^2)_3$, a procatalyst, an optional co-catalyst, and an optional solvent, and (b) recovering a product comprising the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$, wherein step (a) is conducted at a temperature from 1°C to 50 °C, or from 10°C to 40 °C, or from 20°C to 30°C for a time of 1 to 50 hours, or from 10 to 40 hours, or from 15 to 25 hours, and wherein: Y^2 at each occurrence independently is a C_1 to C_{30} hydrocarbyl group; and A^2 at each occurrence independently is a hydrocarbyl group comprising a hindered double bond.

[0125] For the catalytic process of preparing the organoaluminum compound of the formula $Al(CH_2CH(Y^2)A^2)_3$, Y^2 will be a C_1 to C_{30} hydrocarbyl group while A^2 may be any of the previously described embodiments. Each of the procatalyst, the optional co-catalyst, and the optional solvent may be any disclosed herein. The starting materials in step (a) may comprise a ratio of the aluminum alkyl of the formula $Al(Y^2)_3$ to the hydrocarbon of the formula $CH_2=CHA^2$ of from 1:10, or 1:5, or 1:3. The starting materials in step (a) may comprise one or more hydrocarbons of the formula $CH_2=CHA^2$, wherein: A^2 at each occurrence of each hydrocarbon independently is a hydrocarbyl group comprising a hindered double bond; and the starting materials comprise a ratio of the aluminum alkyl of the formula $Al(Y^2)_3$ to the one or more hydrocarbons of the formula $CH_2=C(Y^2)A^2$ of from 1:10, or 1:5, or 1:3. In certain embodiments, Y^2 may be a C_1 to C_{10} alkyl group, and A^2 may be selected from among (AA) to (AZ) and (AZ1) discussed previously. In further embodiments, A^2 may be selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1). The pendant methyl group of (AF) may be connected to any carbon atom that is a ring member.

The (c1) catalyst component

[0126] In certain embodiments, the (c1) catalyst component comprises a procatalyst. In these embodiments, the procatalyst becomes an active catalyst to polymerize unsaturated monomers without a co-catalyst. In further embodiments, the (c1) catalyst component comprises a

procatalyst and a co-catalyst, whereby an active catalyst is formed by the combination of the procatalyst and the co-catalyst. In these embodiments, the (c1) active catalyst component may comprise a ratio of the procatalyst to the co-catalyst of 1:2, or 1:1.5, or 1:1.2.

[0127] Suitable procatalysts include but are not limited to those disclosed in WO 2005/090426, WO 2005/090427, WO 2007/035485, WO 2009/012215, WO 2014/105411, WO 2017/173080, U.S. Patent Publication Nos. 2006/0199930, 2007/0167578, 2008/0311812, and U.S. Patent Nos. 7,858,706 B2, 7,355,089 B2, 8,058,373 B2, and 8,785,554 B2. With reference to the paragraphs below, the term "procatalyst" is interchangeable with the terms "catalyst," "precatalyst," "catalyst precursor," "transition metal catalyst," "transition metal catalyst precursor," "polymerization catalyst," "polymerization catalyst precursor," "transition metal complex," "transition metal compound," "metal complex," "metal compound," "complex," and "metal-ligand complex," and like terms.

[0128] Both heterogeneous and homogeneous catalysts may be employed. Examples of heterogeneous catalysts include the well known Ziegler-Natta compositions, especially Group 4 metal halides supported on Group 2 metal halides or mixed halides and alkoxides and the well known chromium or vanadium based catalysts. Preferably, the catalysts for use herein are homogeneous catalysts comprising a relatively pure organometallic compound or metal complex, especially compounds or complexes based on metals selected from Groups 3-10 or the Lanthanide series of the Periodic Table of the Elements.

[0129] Metal complexes for use herein may be selected from Groups 3 to 15 of the Periodic Table of the Elements containing one or more delocalized, π-bonded ligands or polyvalent Lewis base ligands. Examples include metallocene, half-metallocene, constrained geometry, and polyvalent pyridylamine, or other polychelating base complexes. The complexes are generically depicted by the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein

M is a metal selected from Groups 3-15, preferably 3-10, more preferably 4-10, and most preferably Group 4 of the Periodic Table of the Elements;

K independently at each occurrence is a group containing delocalized π-electrons or one or more electron pairs through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two or more K groups may be joined together forming a bridged structure, and further optionally one or more K groups may be bound to Z, to X or to both Z and X;

X independently at each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X groups may be bonded together thereby forming a divalent or polyvalent anionic group, and, further optionally, one or more X groups and one or more Z groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto; or two X groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π-electrons to M, whereupon M is in the +2 formal oxidation state, and

Z independently at each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3; x is an integer from 1 to 4; z is a number from 0 to 3; and the sum, k+x, is equal to the formal oxidation state of M.

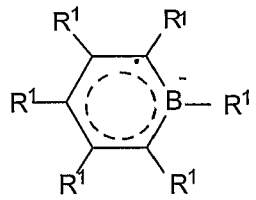
[0130] Suitable metal complexes include those containing from 1 to 3 π-bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized π-bonded anionic ligand groups. Exemplary of such π-bonded groups are conjugated or nonconjugated, cyclic or non-cyclic diene and dienyl groups, allyl groups, boratabenzene groups, phosphole, and arene groups. By the term "π-bonded" is meant that the ligand group is bonded to the transition metal by a sharing of electrons from a partially delocalized π-bond.

[0131] Each atom in the delocalized π-bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted heteroatoms wherein the heteroatom is selected from Group 14-16 of the Periodic Table of the Elements, and such hydrocarbyl-substituted heteroatom radicals further substituted with a Group 15 or 16 hetero atom containing moiety. In addition, two or more such radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems, or they may form a metallocycle with the metal. Included within the term "hydrocarbyl" are C_{1-20} straight, branched and cyclic alkyl radicals, C_{6-20} aromatic radicals, C_{7-20} alkyl-substituted aromatic radicals, and C_{7-20} aryl-substituted alkyl radicals. Suitable hydrocarbyl-substituted heteroatom radicals include mono-, di- and tri-substituted radicals of boron, silicon, germanium, nitrogen, phosphorus or oxygen wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples include N,N-dimethylamino, pyrrolidinyl,

trimethylsilyl, triethylsilyl, t-butyldimethylsilyl, methyldi(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amino, phosphino, alkoxy, or alkylthio moieties or divalent derivatives thereof, for example, amide, phosphide, alkyleneoxy or alkylenethio groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group, π-bonded group, or hydrocarbyl-substituted heteroatom.

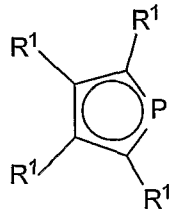
[0132] Examples of suitable anionic, delocalized π-bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, phosphole, and boratabenzyl groups, as well as inertly substituted derivatives thereof, especially C_{1-10} hydrocarbyl- substituted or tris(C_{1-10} hydrocarbyl)silyl- substituted derivatives thereof. Preferred anionic delocalized π-bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, 1- indacenyl, 3-pyrrolidinoinden-1-yl, 3,4-(cyclopenta(1)phenanthren-1-yl, and tetrahydroindenyl.

[0133] The boratabenzenyl ligands are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenyl ligands correspond to the formula:



wherein R^1 is an inert substituent, preferably selected from the group consisting of hydrogen, hydrocarbyl, silyl, halo or germyl, said R^1 having up to 20 atoms not counting hydrogen, and optionally two adjacent R^1 groups may be joined together. In complexes involving divalent derivatives of such delocalized π-bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.

[0134] Phospholes are anionic ligands that are phosphorus containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:



wherein R^1 is as previously defined.

[0135] Suitable transition metal complexes for use herein correspond to the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein:

M is a Group 4 metal;

K is a group containing delocalized π-electrons through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two K groups may be joined together forming a bridged structure, and further optionally one K may be bound to X or Z;

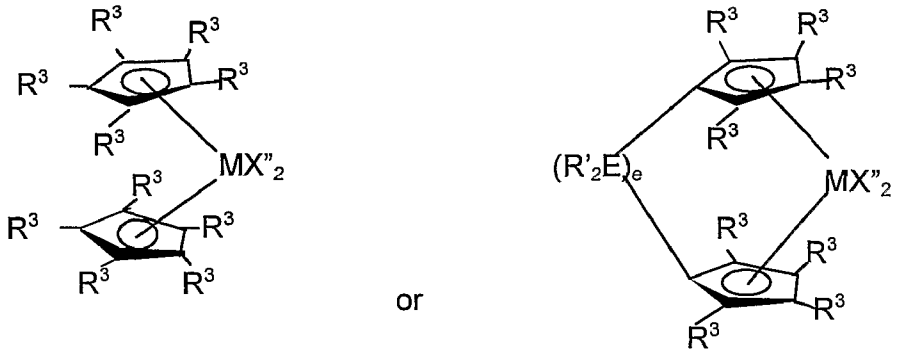
X at each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X and one or more K groups are bonded together to form a metallocycle, and further optionally one or more X and one or more Z groups are bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto;

Z independently at each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3; x is an integer from 1 to 4; z is a number from 0 to 3; and the sum, k+x, is equal to the formal oxidation state of M.

[0136] Suitable complexes include those containing either one or two K groups. The latter complexes include those containing a bridging group linking the two K groups. Suitable bridging groups are those corresponding to the formula $(ER'_2)_e$ wherein E is silicon, germanium, tin, or carbon, R' independently at each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms, and e is 1 to 8. Illustratively, R' independently at each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

[0137] Examples of the complexes containing two K groups are compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state; R^3 at each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non- hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

X" independently at each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X" groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π-electrons to M, whereupon M is in the +2 formal oxidation state, and R', E and e are as previously defined.

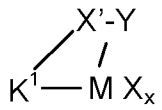
[0138] Exemplary bridged ligands containing two π-bonded groups are: dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane, dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-t-butylcyclopentadien-1-yl)silane, 2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane, dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(fluoren-1-yl)silane, dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)-silane, dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane, dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane, dimethyl(cyclopentadienyl)(tetrahydrofluoren-1-yl)silane, (1,1,2,2-tetramethy)-1,2-bis(cyclopentadienyl)disilane, (1,2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-1-(fluoren-1-yl)methane.

[0139] Suitable X" groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl groups, or two X" groups together form a divalent derivative of a conjugated diene or else together they form a neutral, π-bonded, conjugated diene. Exemplary X" groups are C1-20 hydrocarbyl groups.

[0140] A further class of metal complexes utilized in the present disclosure corresponds to the preceding formula: MKZ_zX_x, or a dimer thereof, wherein M, K, X, x and z are as previously defined, and Z is a substituent of up to 50 non-hydrogen atoms that together with K forms a metallocycle with M.

[0141] Suitable Z substituents include groups containing up to 30 non-hydrogen atoms comprising at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the Elements directly attached to K, and a different atom, selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

[0142] More specifically this class of Group 4 metal complexes used according to the present invention includes "constrained geometry catalysts" corresponding to the formula:



wherein: M is titanium or zirconium, preferably titanium in the +2, +3, or +4 formal oxidation state;

K^1 is a delocalized, π-bonded ligand group optionally substituted with from 1 to 5 R^2 groups,

R^2 at each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^2 having up to 20 non-hydrogen atoms, or adjacent R^2 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

each X is a halo, hydrocarbyl, heterohydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two X groups together form a neutral C5-30 conjugated diene or a divalent derivative thereof;

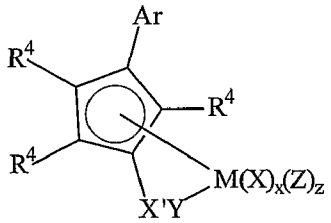
x is 1 or 2;

Y is -O-, -S-, -NR'-, -PR'-;

and X' is SiR'_2, CR'_2, $SiR'_2SiR'_2$, $CR'_2CR'_2$, CR'=CR', $CR'_2SiR'_2$, or GeR'_2, wherein

R' independently at each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms.

[0143] Specific examples of the foregoing constrained geometry metal complexes include compounds corresponding to the formula:



wherein,

Ar is an aryl group of from 6 to 30 atoms not counting hydrogen;

R^4 independently at each occurrence is hydrogen, Ar, or a group other than Ar selected from hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylgermyl, halide, hydrocarbyloxy, trihydrocarbylsiloxy, bis(trihydrocarbylsilyl)amino, di(hydrocarbyl)amino, hydrocarbadiylamino, hydrocarbylimino, di(hydrocarbyl)phosphino, hydrocarbadiylphosphino, hydrocarbylsulfido, halo- substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbylsilyl- substituted hydrocarbyl, trihydrocarbylsiloxy- substituted hydrocarbyl, bis(trihydrocarbylsilyl)amino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino- substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R group having up to 40 atoms not counting hydrogen atoms, and optionally two adjacent R^4 groups may be joined together forming a polycyclic fused ring group;

M is titanium;

X' is SiR^6_2, CR^6_2, $SiR^6_2SiR^6_2$, $CR^6_2CR^6_2$, $CR^6{=}CR^6$, $CR^6_2SiR^6_2$, BR^6, BR^6L'', or GeR^6_2;

Y is -O-, -S-, $-NR^5-$, $-PR^5-$; $-NR^5_2$, or $-PR^5_2$;

R^5, independently at each occurrence is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R^5 having up to 20 atoms other than hydrogen, and optionally two R^5 groups or R^5 together with Y or Z form a ring system;

R^6, independently at each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, $-NR^5_2$, and

combinations thereof, said R^6 having up to 20 non-hydrogen atoms, and optionally, two R^6 groups or R^6 together with Z forms a ring system;

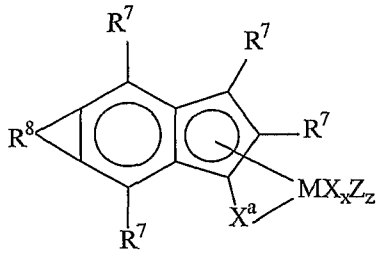
Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to R^5, R^6, or X;

X is hydrogen, a monovalent anionic ligand group having up to 60 atoms not counting hydrogen, or two X groups are joined together thereby forming a divalent ligand group;

x is 1 or 2; and

z is 0, 1 or 2.

[0144] Additional examples of suitable metal complexes herein are polycyclic complexes corresponding to the formula:



where M is titanium in the +2, +3 or +4 formal oxidation state;

R^7 independently at each occurrence is hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R^7 group having up to 40 atoms not counting hydrogen, and optionally two or more of the foregoing groups may together form a divalent derivative;

R^8 is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R^8 containing from 1 to 30 atoms not counting hydrogen;

X^a is a divalent moiety, or a moiety comprising one π-bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said X^a comprising boron, or a member of

Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

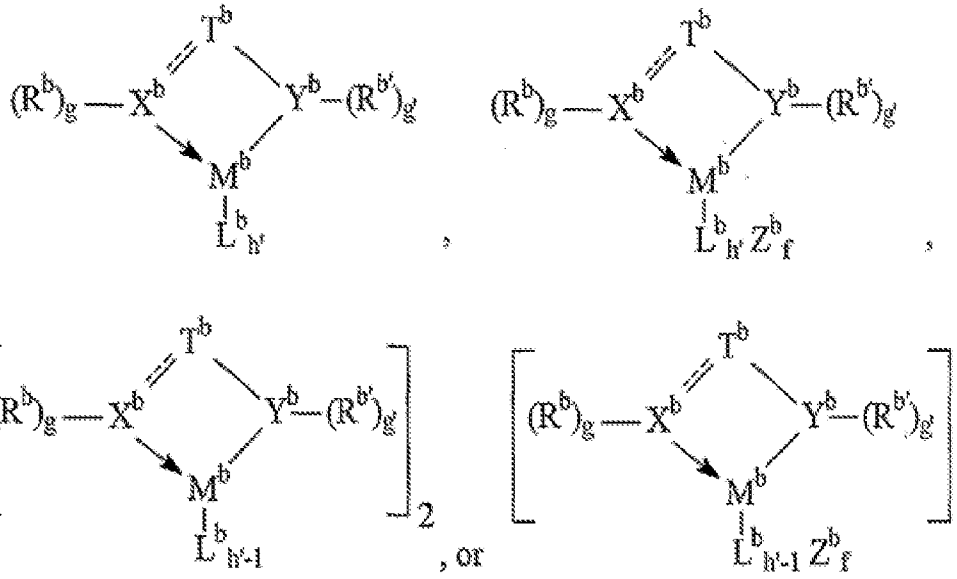
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π-bound ligand groups and optionally two X groups together form a divalent ligand group;

Z independently at each occurrence is a neutral ligating compound having up to 20 atoms;

x is 0, 1 or 2; and

z is zero or 1.

[0145] Additional examples of metal complexes that are usefully employed as catalysts are complexes of polyvalent Lewis bases, such as compounds corresponding to the formula:



wherein T^b is a bridging group, preferably containing 2 or more atoms other than hydrogen,

X^b and Y^b are each independently selected from the group consisting of nitrogen, sulfur, oxygen and phosphorus; more preferably both X^b and Y^b are nitrogen,

R^b and $R^{b'}$ independently each occurrence are hydrogen or C_{1-50} hydrocarbyl groups optionally containing one or more heteroatoms or inertly substituted derivative thereof. Non-limiting examples of suitable R^b and $R^{b'}$ groups include alkyl, alkenyl, aryl, aralkyl,

(poly)alkylaryl and cycloalkyl groups, as well as nitrogen, phosphorus, oxygen and halogen substituted derivatives thereof. Specific examples of suitable R^b and $R^{b'}$ groups include methyl, ethyl, isopropyl, octyl, phenyl, 2,6-dimethylphenyl, 2,6-di(isopropyl)phenyl, 2,4,6-trimethylphenyl, pentafluorophenyl, 3,5-trifluoromethylphenyl, and benzyl;

g and g' are each independently 0 or 1;

M^b is a metallic element selected from Groups 3 to 15, or the Lanthanide series of the Periodic Table of the Elements. Preferably, M^b is a Group 3-13 metal, more preferably M^b is a Group 4-10 metal;

L^b is a monovalent, divalent, or trivalent anionic ligand containing from 1 to 50 atoms, not counting hydrogen. Examples of suitable L^b groups include halide; hydride; hydrocarbyl, hydrocarbyloxy; di(hydrocarbyl)amido, hydrocarbyleneamido, di(hydrocarbyl)phosphido; hydrocarbylsulfido; hydrocarbyloxy, tri(hydrocarbylsilyl)alkyl; and carboxylates. More preferred L^b groups are C1-20 alkyl, C_{7-20} aralkyl, and chloride;

h and h' are each independently an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3, and j is 1 or 2, with the value h x j selected to provide charge balance;

Z^b is a neutral ligand group coordinated to M^b, and containing up to 50 atoms not counting hydrogen. Preferred Z^b groups include aliphatic and aromatic amines, phosphines, and ethers, alkenes, alkadienes, and inertly substituted derivatives thereof. Suitable inert substituents include halogen, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, di(hydrocarbyl)amine, tri(hydrocarbyl)silyl, and nitrile groups. Preferred Z^b groups include triphenylphosphine, tetrahydrofuran, pyridine, and 1,4-diphenylbutadiene;

f is an integer from 1 to 3;

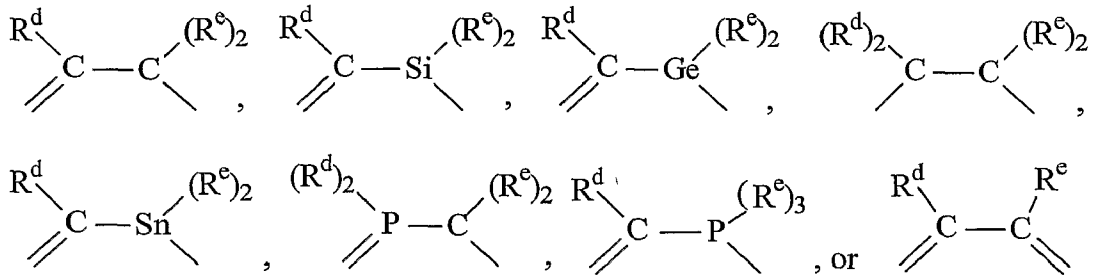
two or three of T^b, R^b and $R^{b'}$ may be joined together to form a single or multiple ring structure;

h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3;

[0146] In one embodiment, it is preferred that R^b have relatively low steric hindrance with respect to X^b. In this embodiment, most preferred R^b groups are straight chain alkyl groups, straight chain alkenyl groups, branched chain alkyl groups wherein the closest branching point is at least 3 atoms removed from X^b, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl

substituted derivatives thereof. Highly preferred R^b groups in this embodiment are C1-8 straight chain alkyl groups.

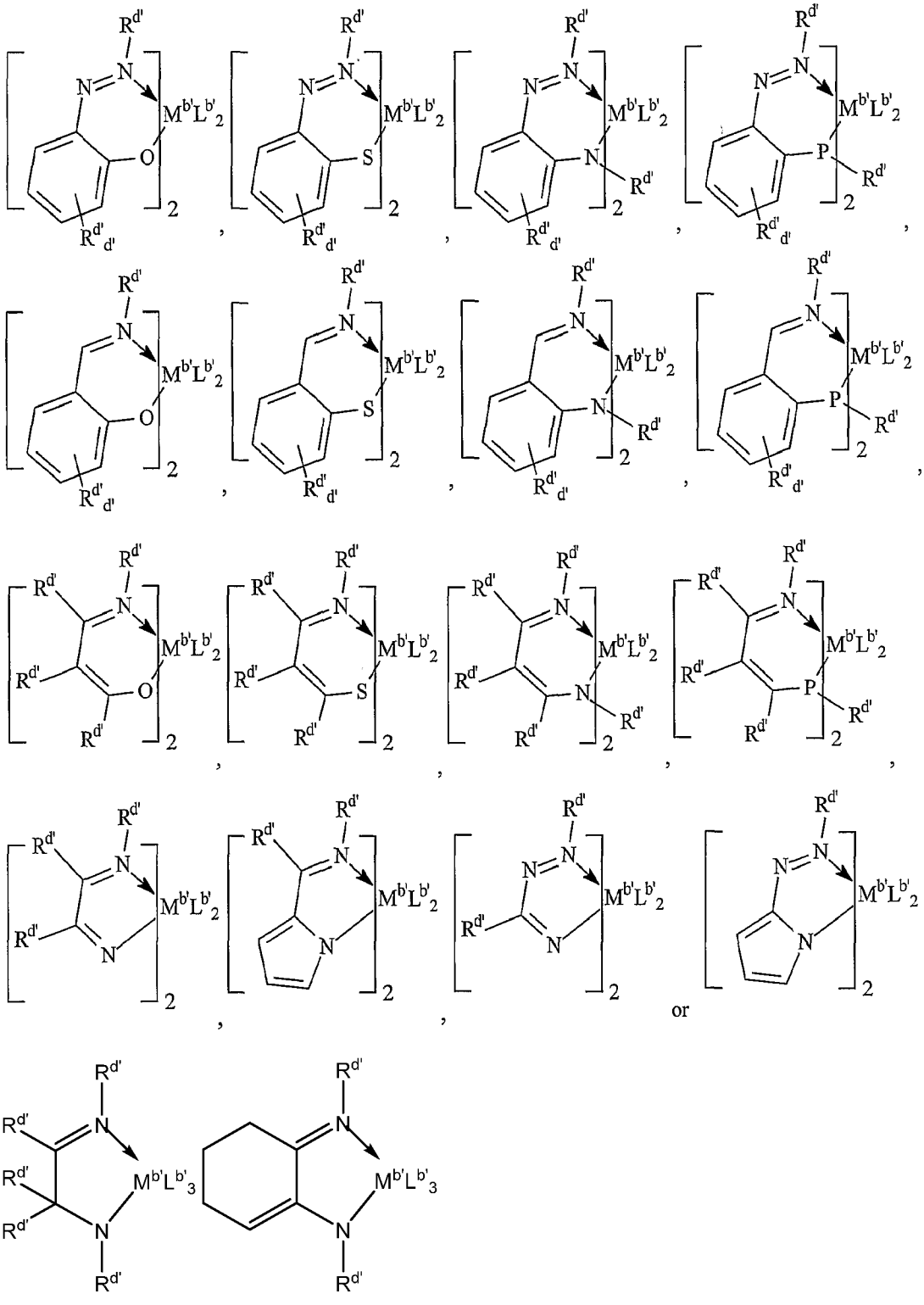
[0147] At the same time, in this embodiment $R^{b'}$ preferably has relatively high steric hindrance with respect to Y^b. Non-limiting examples of suitable $R^{b'}$ groups for this embodiment include alkyl or alkenyl groups containing one or more secondary or tertiary carbon centers, cycloalkyl, aryl, alkaryl, aliphatic or aromatic heterocyclic groups, organic or inorganic oligomeric, polymeric or cyclic groups, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives thereof. Preferred $R^{b'}$ groups in this embodiment contain from 3 to 40, more preferably from 3 to 30, and most preferably from 4 to 20 atoms not counting hydrogen and are branched or cyclic. Examples of preferred T^b groups are structures corresponding to the following formulas:



wherein

Each R^d is C1-10 hydrocarbyl group, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. Each R^e is C1-10 hydrocarbyl, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. In addition, two or more R^d or R^e groups, or mixtures of Rd and Re groups may together form a divalent or polyvalent derivative of a hydrocarbyl group, such as, 1,4-butylene, 1,5-pentylene, or a cyclic ring, or a multicyclic fused ring, polyvalent hydrocarbyl- or heterohydrocarbyl- group, such as naphthalene-1,8-diyl.

[0148] Suitable examples of the foregoing polyvalent Lewis base complexes include:



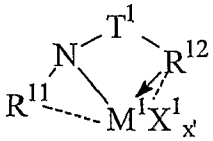
wherein $R^{d'}$ at each occurrence is independently selected from the group consisting of hydrogen and C1-50 hydrocarbyl groups optionally containing one or more heteroatoms, or inertly substituted derivative thereof, or further optionally, two adjacent $R^{d'}$ groups may together form a divalent bridging group;

d' is 4;

$M^{b'}$ is a Group 4 metal, preferably titanium or hafnium, or a Group 10 metal, preferably Ni or Pd;

$L^{b'}$ is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl, or two $L^{b'}$ groups together are a divalent or neutral ligand group, preferably a C_{2-50} hydrocarbylene, hydrocarbadiyl or diene group.

[0149] The polyvalent Lewis base complexes for use in the present invention especially include Group 4 metal derivatives, especially hafnium derivatives of hydrocarbylamine substituted heteroaryl compounds corresponding to the formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

T^1 is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di- C1-20 hydrocarbyl substituted methylene or silane group; and

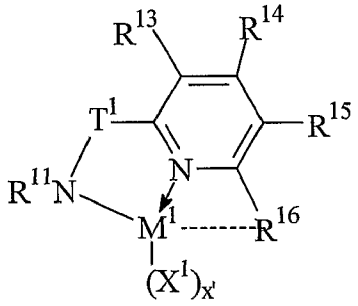
R^{12} is a C_{5-20} heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

M^1 is a Group 4 metal, preferably hafnium;

X^1 is an anionic, neutral or dianionic ligand group;

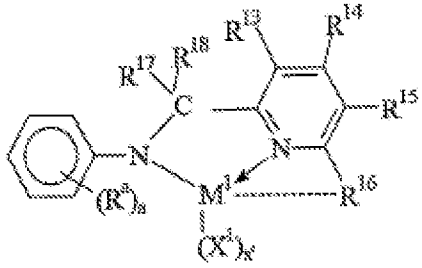
x' is a number from 0 to 5 indicating the number of such X^1 groups; and bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

[0150] Suitable complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from R^{12}. In addition, electron donation from the Lewis base functionality, preferably an electron pair, provides additional stability to the metal center. Suitable metal complexes correspond to the formula:



wherein M^1, X^1, x', R^{11} and T^1 are as previously defined,

R^{13}, R^{14}, R^{15} and R^{16} are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent R^{13}, R^{14}, R^{15} or R^{16} groups may be joined together thereby forming fused ring derivatives, and bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively. Suitable examples of the foregoing metal complexes correspond to the formula:



wherein

M^1, X^1, and x' are as previously defined,

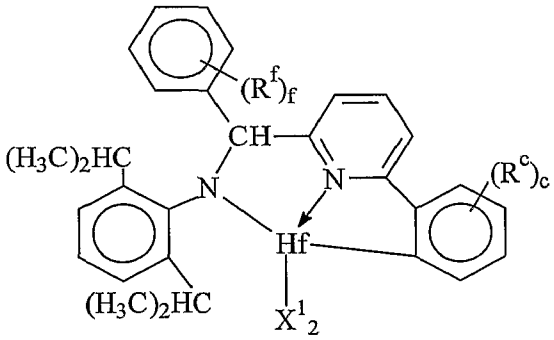
R^{13}, R^{14}, R^{15} and R^{16} are as previously defined, preferably R^{13}, R^{14}, and R^{15} are hydrogen, or C1-4 alkyl, and R^{16} is C_{6-20} aryl, most preferably naphthalenyl;

R^a independently at each occurrence is C_{1-4} alkyl, and a is 1-5, most preferably R^a in two ortho-positions to the nitrogen is isopropyl or t-butyl;

R^{17} and R^{18} independently at each occurrence are hydrogen, halogen, or a C_{1-20} alkyl or aryl group, most preferably one of R^{17} and R^{18} is hydrogen and the other is a C6-20 aryl group,

especially 2-isopropyl, phenyl or a fused polycyclic aryl group, most preferably an anthracenyl group, and bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

[0151] Exemplary metal complexes for use herein as catalysts correspond to the formula:

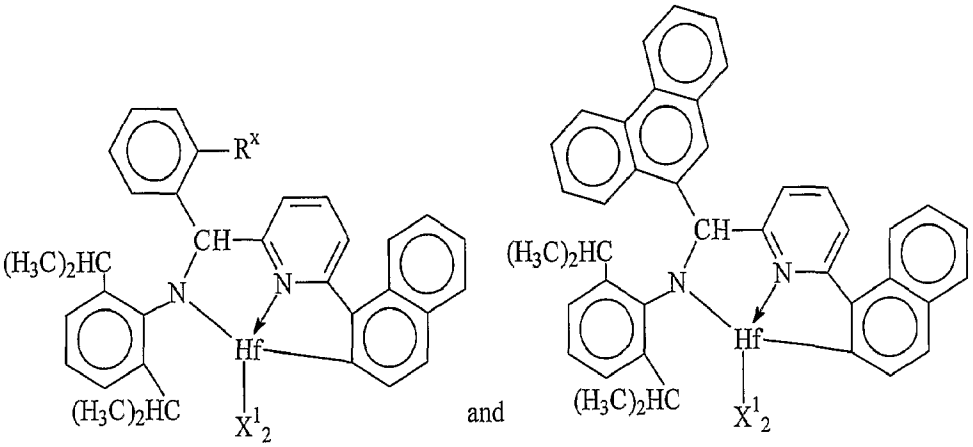


wherein X^1 at each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, and preferably at each occurrence X^1 is methyl;

R^f independently at each occurrence is hydrogen, halogen, C1-20 alkyl, or C6-20 aryl, or two adjacent R^f groups are joined together thereby forming a ring, and f is 1-5; and

R^c independently at each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^c groups are joined together thereby forming a ring, and c is 1-5.

[0152] Suitable examples of metal complexes for use as catalysts according to the present invention are complexes of the following formulas:

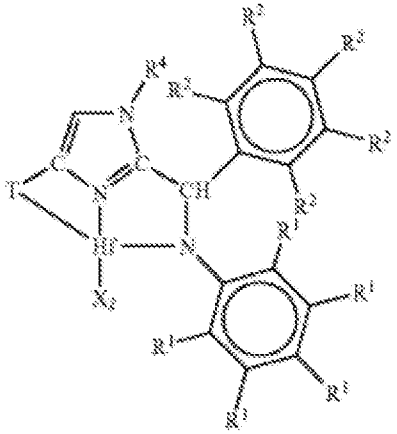


wherein R^x is C1-4 alkyl or cycloalkyl, preferably methyl, isopropyl, t-butyl or cyclohexyl; and X^1 at each occurrence is halide, N,N-dimethylamido, or C1-4 alkyl, preferably methyl.

[0153] Examples of metal complexes usefully employed as catalysts according to the present invention include:
[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;
[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);
[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;
[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;
[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);
[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafhium dimethyl;
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafhium di(N,N-dimethylamido); and
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

[0154] Under the reaction conditions used to prepare the metal complexes used in the present disclosure, the hydrogen of the 2-position of the α-naphthalene group substituted at the 6-position of the pyridin-2-yl group is subject to elimination, thereby uniquely forming metal complexes wherein the metal is covalently bonded to both the resulting amide group and to the 2-position of the α- naphthalenyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair of the nitrogen atom.

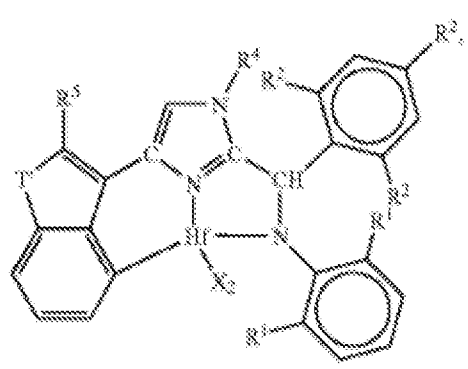
[0155] Further procatalysts that are suitable include imidazole-amine compounds corresponding to those disclosed in WO 2007/130307A2, WO 2007/130306A2, and U.S. Patent Application Publication No. 20090306318A1, which are incorporated herein by reference in their entirety. Such imidazole-amine compounds include those corresponding to the formula:

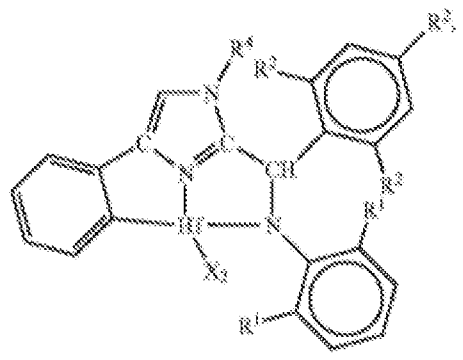


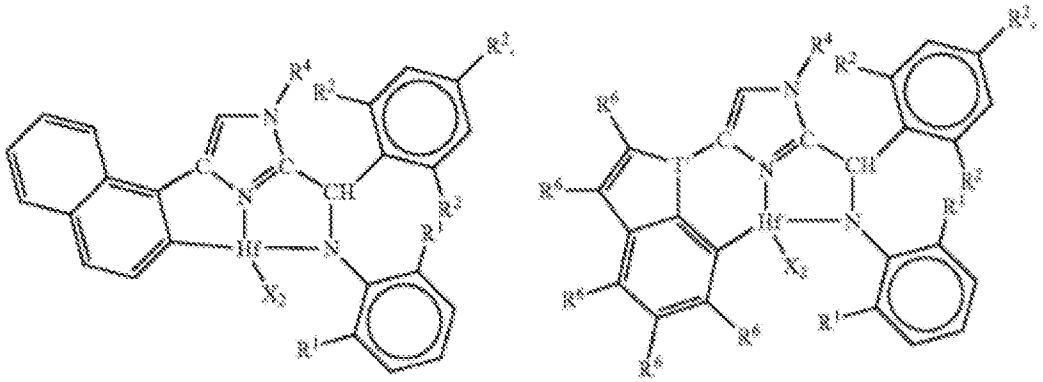
, wherein

X independently each occurrence is an anionic ligand, or two X groups together form a dianionic ligand group, or a neutral diene; T is a cycloaliphatic or aromatic group containing one or more rings; R^1 independently each occurrence is hydrogen, halogen, or a univalent, polyatomic anionic ligand, or two or more R^1 groups are joined together thereby forming a polyvalent fused ring system; R^2 independently each occurrence is hydrogen, halogen, or a univalent, polyatomic anionic ligand, or two or more R^2 groups are joined together thereby forming a polyvalent fused ring system; and R^4 is hydrogen, alkyl, aryl, aralkyl, trihydrocarbylsilyl, or trihydrocarbylsilylmethyl of from 1 to 20 carbons.

[0156] Further examples of such imidazole-amine compounds include but are not limited to the following:



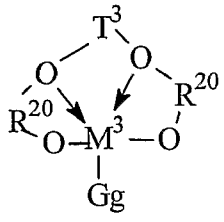




, wherein:

R^1 independently each occurrence is a C_{3-12} alkyl group wherein the carbon attached to the phenyl ring is secondary or tertiary substituted; R^2 independently each occurrence is hydrogen or a C_{1-2} alkyl group; R^4 is methyl or isopropyl; R^5 is hydrogen or C_{1-6} alkyl; R^6 is hydrogen, C_{1-6} alkyl or cycloalkyl, or two adjacent R^6groups together form a fused aromatic ring; T′ is oxygen, sulfur, or aC_{1-20} hydrocarbyl-substituted nitrogen or phosphorus group; T″ is nitrogen or phosphorus; and X is methyl or benzyl.

[0157] Additional suitable metal complexes of polyvalent Lewis bases for use herein include compounds corresponding to the formula:



, wherein:

R^{20} is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

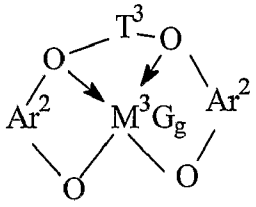
T^3 is a hydrocarbylene or hydrocarbyl silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

M^3 is a Group 4 metal, preferably zirconium or hafnium;

G is an anionic, neutral or dianionic ligand group; preferably a halide, hydrocarbyl, silane, trihydrocarbylsilylhydrocarbyl, trihydrocarbylsilyl, or dihydrocarbylamide group having up to 20 atoms not counting hydrogen;

g is a number from 1 to 5 indicating the number of such G groups; and bonds and electron donative interactions are represented by lines and arrows respectively.

[0158] Illustratively, such complexes correspond to the formula:



, wherein:

T^3 is a divalent bridging group of from 2 to 20 atoms not counting hydrogen, preferably a substituted or unsubstituted, C3-6 alkylene group;

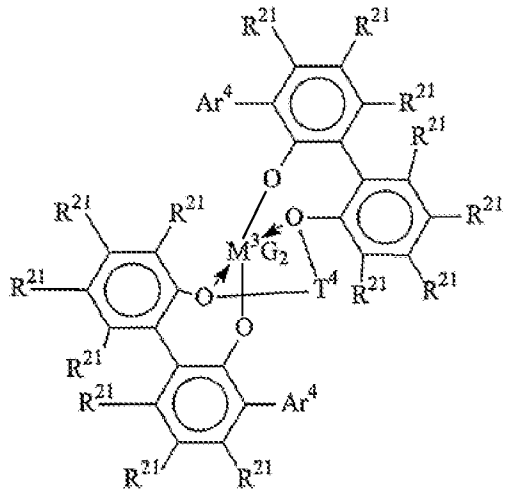
and Ar^2 independently at each occurrence is an arylene or an alkyl- or aryl-substituted arylene group of from 6 to 20 atoms not counting hydrogen;

M^3 is a Group 4 metal, preferably hafnium or zirconium;

G independently at each occurrence is an anionic, neutral or dianionic ligand group;

g is a number from 1 to 5 indicating the number of such X groups; and electron donative interactions are represented by arrows.

[0159] Suitable examples of metal complexes of foregoing formula include the following compounds



where M^3 is Hf or Zr;

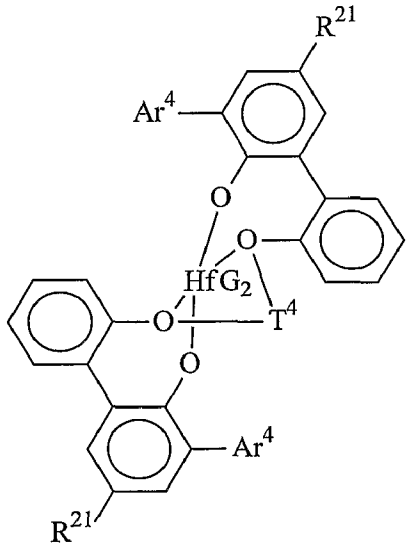
Ar^4 is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl, and

T^4 independently at each occurrence comprises a C_{3-6} alkylene group, a C_{3-6} cycloalkylene group, or an inertly substituted derivative thereof;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl of up to 50 atoms not counting hydrogen; and

G, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 G groups together are a divalent derivative of the foregoing hydrocarbyl or trihydrocarbylsilyl groups.

[0160] Suitable compounds are compounds of the formulas:



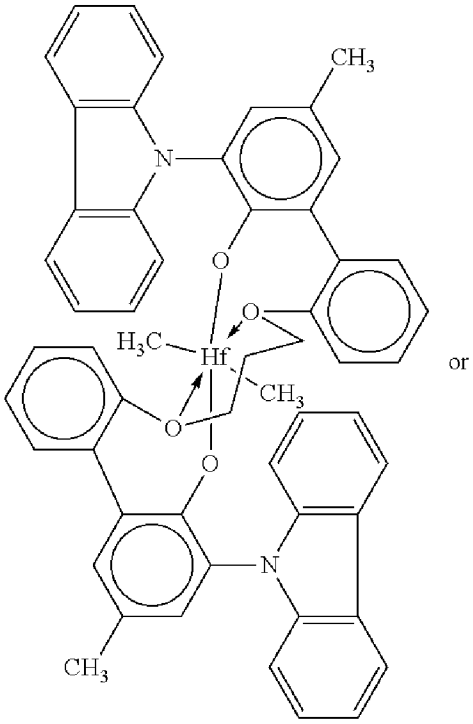
wherein Ar^4 is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R^{21} is hydrogen, halo, or C1-4 alkyl, especially methyl

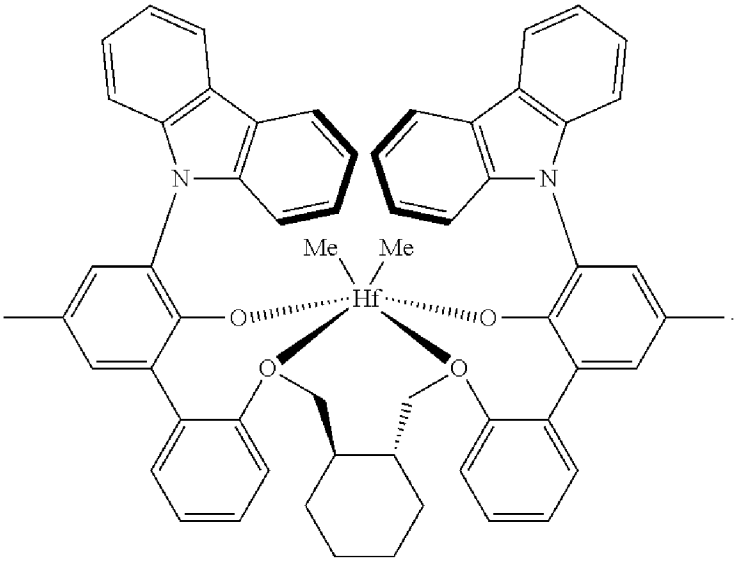
T^4 is propan-1,3-diyl or butan-1,4-diyl, and

G is chloro, methyl or benzyl.

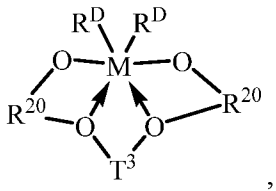
[0161] Exemplary metal complexes of the foregoing formula are:



or



[0162] Suitable metal complexes for use according to the present disclosure further include compounds corresponding to the formula:



, where:

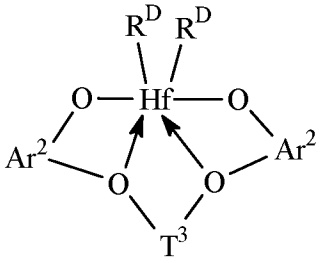
M is zirconium or hafnium;

R^{20} independently at each occurrence is a divalent aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen;

T^3 is a divalent hydrocarbon or silane group having from 3 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof; and

R^D independently at each occurrence is a monovalent ligand group of from 1 to 20 atoms, not counting hydrogen, or two R^D groups together are a divalent ligand group of from 1 to 20 atoms, not counting hydrogen.

[0163] Such complexes may correspond to the formula:



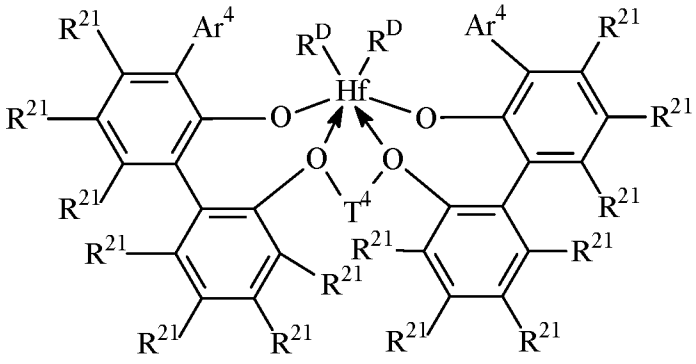
, wherein:

Ar^2 independently at each occurrence is an arylene or an alkyl-, aryl-, alkoxy- or amino-substituted arylene group of from 6 to 20 atoms not counting hydrogen or any atoms of any substituent;

T^3 is a divalent hydrocarbon bridging group of from 3 to 20 atoms not counting hydrogen, preferably a divalent substituted or unsubstituted C_{3-6} aliphatic, cycloaliphatic, or bis(alkylene)-substituted cycloaliphatic group having at least 3 carbon atoms separating oxygen atoms; and

R^D independently at each occurrence is a monovalent ligand group of from 1 to 20 atoms, not counting hydrogen, or two R^D groups together are a divalent ligand group of from 1 to 40 atoms, not counting hydrogen.

[0164] Further examples of metal complexes suitable for use herein include compounds of the formula:



, where

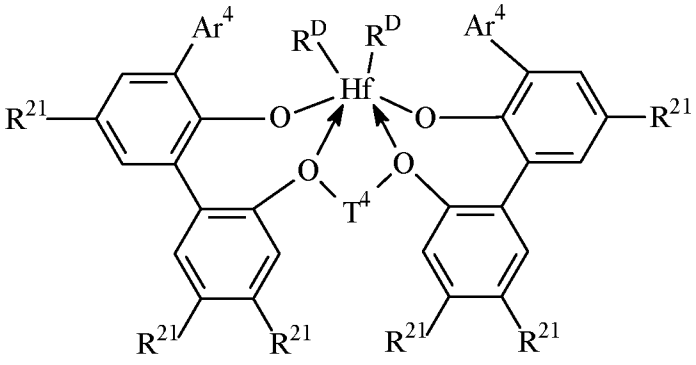
Ar^4 independently at each occurrence is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, naphthyl, anthracen-5-yl, 1,2,3,4,6,7,8,9-octahydroanthracen-5-yl;

T^4 independently at each occurrence is a propylene-1,3-diyl group, a bis(alkylene)cyclohexan-1,2-diyl group, or an inertly substituted derivative thereof substituted with from 1 to 5 alkyl, aryl or aralkyl substituents having up to 20 carbons each;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen; and

R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group of up to 40 atoms not counting hydrogen.

[0165] Exemplary metal complexes are compounds of the formula:

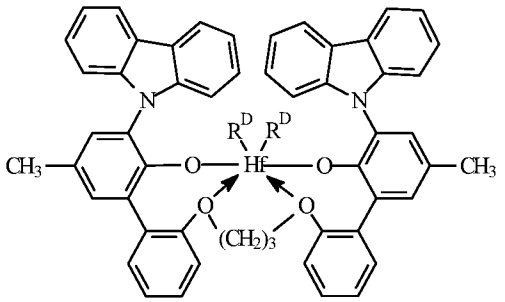
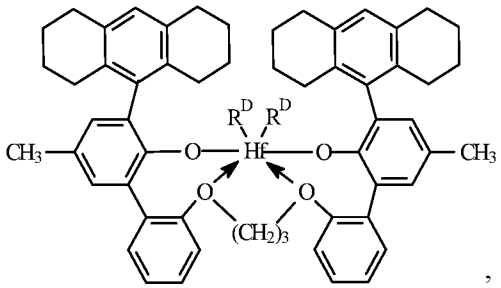
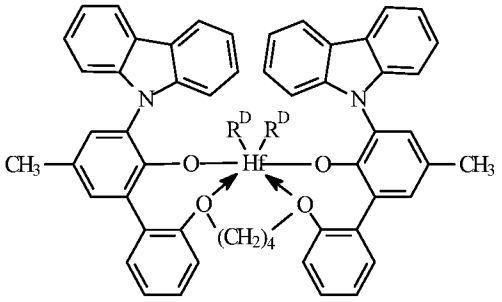
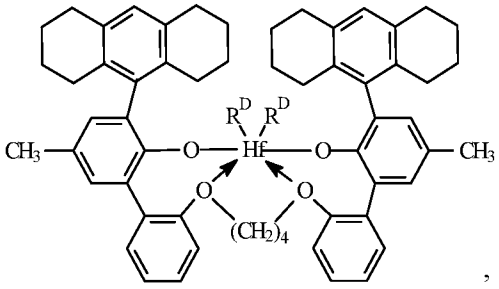
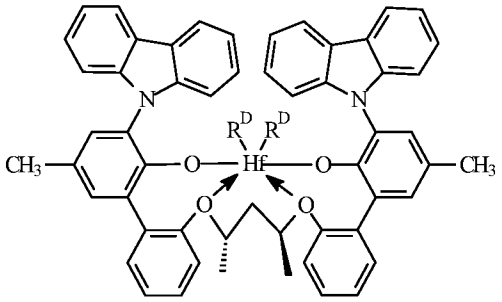
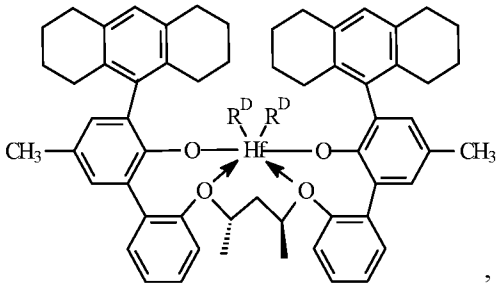
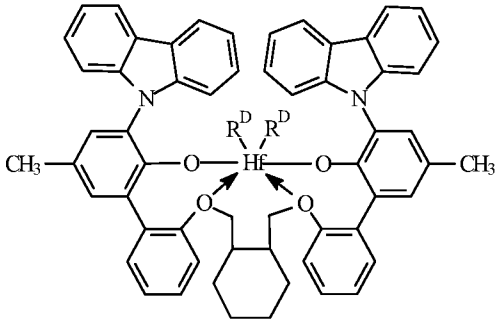
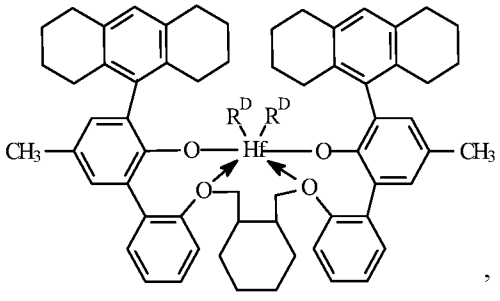


,

where, Ar^4, independently at each occurrence, is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen;
T^4 is propan-1,3-diyl or bis(methylene)cyclohexan-1,2-diyl; and
R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl or hydrocarbylsilanediyl group of up to 40 atoms not counting hydrogen.

[0166] Suitable metal complexes according to the present disclosure correspond to the formulas:


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, or

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wherein, R^D independently at each occurrence is chloro, methyl or benzyl.

[0167] Specific examples of suitable metal complexes are the following compounds:

A) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dimethyl,

bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dichloride,

bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-1,3-propanediylhafnium (IV) dibenzyl,

B) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-1,4-butanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-1,4-butanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-1,4-butanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-1,4-butanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-1,4-butanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-1,4-butanediylhafnium (IV) dibenzyl,

C) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediylhafnium (IV) dimethyl,

bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)-2,4-pentanediylhafnium (IV) dibenzyl,

D) bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dichloride,
bis((2-oxoyl-3-(1,2,3,4,6,7,8,9-octahydroanthracen-5-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dibenzyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dimethyl,
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dichloride, and
bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)-methylenetrans-1,2-cyclohexanediylhafnium (IV) dibenzyl.

[0168] The foregoing metal complexes may be conveniently prepared by standard metallation and ligand exchange procedures involving a source of the transition metal and a neutral polyfunctional ligand source. The techniques employed are the same as or analogous to those disclosed in USP 6,827,976 and US2004/0010103, and elsewhere.

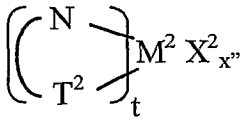
[0169] The foregoing polyvalent Lewis base complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the Group 4 metal and the neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. Other techniques may be used as well. These complexes are known from the disclosures of, among others, US patents 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, and US 04/0220050.

[0170] Catalysts having high comonomer incorporation properties are also known to reincorporate in situ prepared long chain olefins resulting incidentally during the polymerization

through β- hydride elimination and chain termination of growing polymer, or other process. The concentration of such long chain olefins is particularly enhanced by use of continuous solution polymerization conditions at high conversions, especially ethylene conversions of 95 percent or greater, more preferably at ethylene conversions of 97 percent or greater. Under such conditions a small but detectable quantity of olefin terminated polymer may be reincorporated into a growing polymer chain, resulting in the formation of long chain branches, that is, branches of a carbon length greater than would result from other deliberately added comonomer. Moreover, such chains reflect the presence of other comonomers present in the reaction mixture. That is, the chains may include short chain or long chain branching as well, depending on the comonomer composition of the reaction mixture. Long chain branching of olefin polymers is further described in USP's 5,272,236, 5,278,272, and 5,665,800.

[0171] Alternatively, branching, including hyper-branching, may be induced in a particular segment of the present multi-block copolymers by the use of specific catalysts known to result in "chain-walking" in the resulting polymer. For example, certain homogeneous bridged bis indenyl- or partially hydrogenated bis indenyl- zirconium catalysts, disclosed by Kaminski, et al., J. Mol. Catal. A: Chemical, 102 (1995) 59-65; Zambelli, et al., Macromolecules, 1988, 21, 617-622; or Dias, et al., J. Mol. Catal. A: Chemical, 185 (2002) 57-64 may be used to prepare branched copolymers from single monomers, including ethylene.

[0172] Additional complexes suitable for use include Group 4-10 derivatives corresponding to the formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements, preferably Group 4 metals, Ni(II) or Pd(II), most preferably zirconium;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

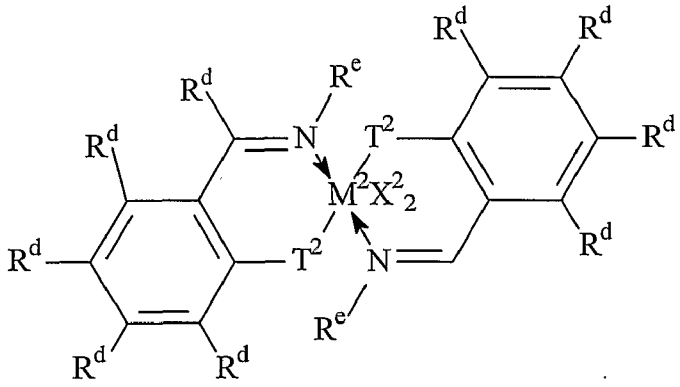
t is one or two;

x" is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

Such catalysts have been previously disclosed in J. Am. Chem. Soc., 118, 267-268 (1996), J. Am. Chem. Soc., 117, 6414 -6415 (1995), and Organometallics, 16, 1514-1516, (1997), among other disclosures.

[0173] Suitable examples of the foregoing metal complexes for use as catalysts are aromatic diimine or aromatic dioxyimine complexes of Group 4 metals, especially zirconium, corresponding to the formula:



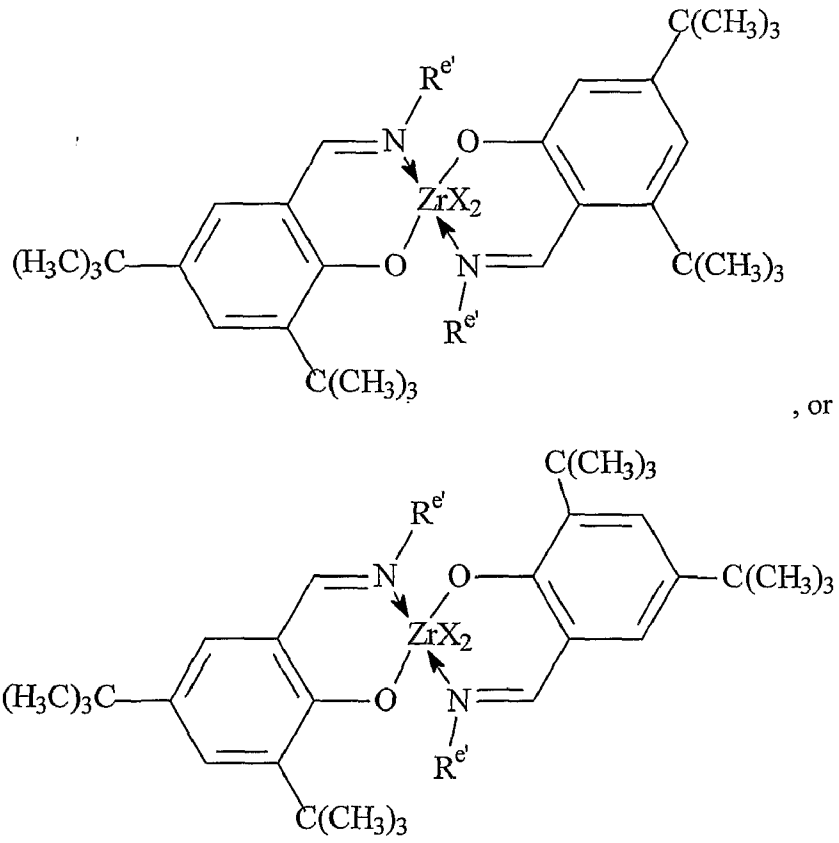
wherein;

M^2, X^2 and T^2 are as previously defined;

R^d independently in each occurrence is hydrogen, halogen, or R^e; and

R^e independently in each occurrence is C1-20 hydrocarbyl or a heteroatom-, especially a F, N, S or P- substituted derivative thereof, more preferably C1-20 hydrocarbyl or a F or N substituted derivative thereof, most preferably alkyl, dialkylaminoalkyl, pyrrolyl, piperidenyl, perfluorophenyl, cycloalkyl, (poly)alkylaryl, or aralkyl.

[0174] Suitable examples of the foregoing metal complexes for use as catalysts are aromatic dioxyimine complexes of zirconium, corresponding to the formula:



wherein;

X^2 is as previously defined, preferably C1-10 hydrocarbyl, most preferably methyl or benzyl; and

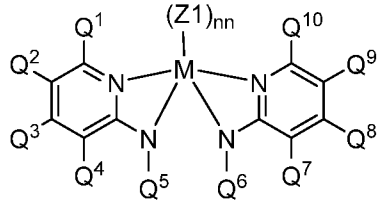
$R^{e'}$ is methyl, isopropyl, t-butyl, cyclopentyl, cyclohexyl, 2-metlıylcyclohexyl, 2,4-dimethylcyclohexyl, 2-pyrrolyl, N-methyl-2-pyrrolyl, 2-piperidenyl, N-methyl-2-piperidenyl, benzyl, o-tolyl, 2,6-dimethylphenyl, perfluorophenyl, 2,6-di(isopropyl)phenyl, or 2,4,6-trimethylphenyl.

[0175] The foregoing complexes for use as also include certain phosphinimine complexes are disclosed in EP-A-890581. These complexes correspond to the formula: $[(R^f)_3\text{-}P{=}N]_fM(K^2)(R^f)_{3-f}$, wherein: R^f is a monovalent ligand or two R^f groups together are a divalent ligand, preferably R^f is hydrogen or C1-4 alkyl;

M is a Group 4 metal,

K^2 is a group containing delocalized π-electrons through which K^2 is bound to M, said K^2 group containing up to 50 atoms not counting hydrogen atoms, and f is 1 or 2.

[0176] Further suitable procatalysts include a those disclosed in WO 2017/173080 A1, which is incorporated by reference in its entirerty. Such procatalysts include the metal-ligand complex of Formula (i):



(i),

wherein M is titanium, zirconium, or hafnium;

wherein each Z1 is independently a monodentate or polydentate ligand that is neutral, monoanionic, or dianionic, wherein nn is an integer, and wherein Z1 and nn are chosen in such a way that the metal-ligand complex of Formula (i) is overall neutral;

wherein each Q^1 and Q^{10} independently is selected from the group consisting of (C_6-C_{40})aryl, substituted (C_6-C_{40})aryl, (C_3-C_{40})heteroaryl, and substituted (C_3-C_{40})heteroaryl;

wherein each Q^2, Q^3, Q^4, Q^7, Q^8, and Q^9 independently is selected from a group consisting of hydrogen, (C_1-C_{40})hydrocarbyl, substituted (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, substituted (C_1-C_{40})heterohydrocarbyl, halogen, and nitro (NO_2);

wherein each Q^5 and Q^6 independently is selected from the group consisting of a (C_1-C_{40})alkyl, substituted (C_1-C_{40})alkyl, and [$(Si)_1$-$(C+Si)_{40}$] substituted organosilyl;

wherein each N independently is nitrogen;

optionally, two or more of the Q^{1-5} groups can combine together to form a ring structure, with such ring structure having from 5 to 16 atoms in the ring excluding any hydrogen atoms; and

optionally, two or more of the Q^{6-10} groups can combine together to form a ring structure, with such ring structure having from 5 to 16 atoms in the ring excluding any hydrogen atoms.

[0177] The metal ligand complex of Formula (i) above, and all specific embodiments thereof herein, is intended to include every possible stereoisomer, including coordination isomers, thereof.

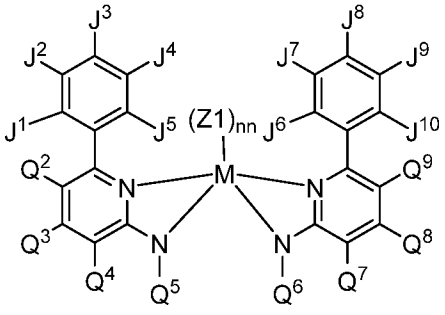
[0178] The metal ligand complex of Formula (i) above provides for homoleptic as well as heteroleptic procatalyst components.

[0179] In an alternative embodiment, each of the (C_1-C_{40}) hydrocarbyl and (C_1-C_{40}) heterohydrocarbyl of any one or more of Q^1, Q^2, Q^3, Q^4, Q^5, Q^6, Q^7, Q^8, Q^9 and Q^{10} each independently is unsubstituted or substituted with one or more R^S substituents, and wherein each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C_1-C_{18})alkyl, (C_6-C_{18})aryl, F_3C, FCH_2O, F_2HCO, F_3CO, $(R^{C1})_3Si$, $(R^{C1})_3Ge$, $(R^{C1})O$, $(R^{C1})S$, $(R^{C1})S(O)$, $(R^{C1})S(O)_2$, $(R^{C1})_2P$, $(R^{C1})_2N$, $(R^{C1})_2C{=}N$, NC, NO_2, $(R^{C1})C(O)O$, $(R^{C1})OC(O)$, $(R^{C1})C(O)N(R^{C1})$, or $(R^{C1})_2NC(O)$, or two of the R^S are taken together to form an unsubstituted (C_1-C_{18})alkylene where each R^S independently is an unsubstituted (C_1-C_{18})alkyl, and wherein independently each R^{C1} is hydrogen, unsubstituted (C_1-C_{18})hydrocarbyl or an unsubstituted (C_1-C_{18})heterohydrocarbyl, or absent (e.g., absent when N comprises -N=). In particular embodiments, Q^5 and Q^6 are each independently (C_1-C_{40}) primary or secondary alkyl groups with respect to their connection to the amine nitrogen of the parent ligand structure. The terms primary and secondary alkyl groups are given their usual and customary meaning herein; i.e., primary indicating that the carbon atom directly linked to the ligand nitrogen bears at least two hydrogen atoms and secondary indicates that the carbon atom directly linked to the ligand nitrogen bears only one hydrogen atom.

[0180] Optionally, two or more $Q^{1\text{-}5}$ groups or two or more $Q^{6\text{-}10}$ groups each independently can combine together to form ring structures, with such ring structures having from 5 to 16 atoms in the ring excluding any hydrogen atoms.

[0181] In preferred embodiments, Q^5 and Q^6 are each independently (C_1-C_{40}) primary or secondary alkyl groups and most preferably, Q^5 and Q^6 are each independently propyl, isopropyl, neopentyl, hexyl, isobutyl and benzyl.

[0182] In particular embodiments, Q^1 and Q^{10} of the olefin polymerization procatalyst of Formula (i) are substituted phenyl groups; as shown in Formula (ii),



(ii);

wherein J^1-J^{10} are each independently selected from the group consisting of R^S substituents and hydrogen; and wherein each R^S independently is a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C_1-C_{18})alkyl, (C_6-C_{18})aryl, F_3C, FCH_2O, F_2HCO, F_3CO, $(R^{C1})_3Si$, $(R^{C1})_3Ge$, $(R^{C1})O$, $(R^{C1})S$, $(R^{C1})S(O)$, $(R^{C1})S(O)_2$, $(R^{C1})_2P$, $(R^{C1})_2N$, $(R^{C1})_2C=N$, NC, NO_2, $(R^{C1})C(O)O$, $(R^{C1})OC(O)$, $(R^{C1})C(O)N(R^{C1})$, or $(R^{C1})_2NC(O)$, or two of the R^S are taken together to form an unsubstituted (C_1-C_{18})alkylene where each R^S independently is an unsubstituted (C_1-C_{18})alkyl, and wherein independently each R^{C1} is hydrogen, unsubstituted (C_1-C_{18})hydrocarbyl or an unsubstituted (C_1-C_{18})heterohydrocarbyl, or absent (e.g., absent when N comprises -N=). More preferably, J^1, J^5, J^6 and J^{10} of Formula (ii) are each independently selected from the group consisting of halogen atoms, (C_1-C_8) alkyl groups, and (C_1-C_8) alkoxyl groups. Most preferably, J^1, J^5, J^6 and J^{10} of Formula (ii) are each independently methyl; ethyl or isopropyl.

[0183] The term "[$(Si)_1$-$(C+Si)_{40}$] substituted organosilyl" means a substituted silyl radical with 1 to 40 silicon atoms and 0 to 39 carbon atoms such that the total number of carbon plus silicon atoms is between 1 and 40. Examples of [$(Si)_1$-$(C+Si)_{40}$] substituted organosilyl include trimethylsilyl, triisopropylsilyl, dimethylphenylsilyl, diphenylmethylsilyl, triphenylsilyl, and triethylsilyl.

[0184] Preferably, there are no O-O, S-S, or O-S bonds, other than O-S bonds in an S(O) or $S(O)_2$ diradical functional group, in the metal-ligand complex of Formula (i). More preferably, there are no O-O, P-P, S-S, or O-S bonds, other than O-S bonds in an S(O) or $S(O)_2$ diradical functional group, in the metal-ligand complex of Formula (i).

[0185] M is titanium, zirconium, or hafnium. In one embodiment, M is titanium. In another embodiment, M is zirconium. In another embodiment, M is hafnium. In some embodiments, M is in a formal oxidation state of +2, +3, or +4. Each Z1 independently is a monodentate or polydentate ligand that is neutral, monoanionic, or dianionic. Z1 and nn are chosen in such a way that the metal-ligand complex of Formula (i) is, overall, neutral. In some embodiments each Z1 independently is the monodentate ligand. In one embodiment when there are two or more Z1 monodentate ligands, each Z1 is the same. In some embodiments the monodentate ligand is the monoanionic ligand. The monoanionic ligand has a net formal oxidation state of -1. Each monoanionic ligand may independently be hydride, (C_1-C_{40})hydrocarbyl carbanion,

(C_1-C_{40})heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, borate, borohydride, sulfate, $HC(O)O^-$, alkoxide or aryloxide (RO^-), (C_1-C_{40})hydrocarbylC(O)O^-, $HC(O)N(H)^-$,(C_1-C_{40})hydrocarbylC(O)$N(H)^-$, (C_1-C_{40})hydrocarbylC(O)$N((C_1$-$C_{20})$hydrocarbyl)$^-$, $R^KR^LB^-$, $R^KR^LN^-$, R^KO^-, R^KS^-, $R^KR^LP^-$, or $R^MR^KR^LSi^-$, wherein each R^K, R^L, and R^M independently is hydrogen, (C_1-C_{40})hydrocarbyl, or (C_1-C_{40})heterohydrocarbyl, or R^K and R^L are taken together to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene and R^M is as defined above.

[0186] In some embodiments at least one monodentate ligand of Z1 independently is the neutral ligand. In one embodiment, the neutral ligand is a neutral Lewis base group that is $R^{X1}NR^KR^L$, R^KOR^L, R^KSR^L, or $R^{X1}PR^KR^L$, wherein each R^{X1} independently is hydrogen, (C_1-C_{40})hydrocarbyl, $[(C_1$-$C_{10})$hydrocarbyl$]_3Si$, $[(C_1$-$C_{10})$hydrocarbyl$]_3Si(C_1$-$C_{10})$hydrocarbyl, or (C_1-C_{40})heterohydrocarbyl and each R^K and R^L independently is as defined above.

[0187] In some embodiments, each Z1 is a monodentate ligand that independently is a halogen atom, unsubstituted (C_1-C_{20})hydrocarbyl, unsubstituted (C_1-C_{20})hydrocarbylC(O)O-, or R^KR^LN- wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{20})hydrocarbyl. In some embodiments each monodentate ligand Z1 is a chlorine atom, (C_1-C_{10})hydrocarbyl (e.g., (C_1-C_6)alkyl or benzyl), unsubstituted (C_1-C_{10})hydrocarbylC(O)O-, or R^KR^LN- wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{10})hydrocarbyl.

[0188] In some embodiments there are at least two Z1s and the two Z1s are taken together to form the bidentate ligand. In some embodiments the bidentate ligand is a neutral bidentate ligand. In one embodiment, the neutral bidentate ligand is a diene of Formula $(R^{D1})_2C=C(R^{D1})$-$C(R^{D1})=C(R^{D1})_2$, wherein each R^{D1} independently is H, unsubstituted (C_1-C_6)alkyl, phenyl, or naphthyl. In some embodiments the bidentate ligand is a monoanionic-mono(Lewis base) ligand. The monoanionic-mono(Lewis base) ligand may be a 1,3-dionate of Formula (D): R^{E1}-$C(O^-)=CH$-$C(=O)$-R^{E1} (D), wherein each R^{E1} independently is H, unsubstituted (C_1-C_6)alkyl, phenyl, or naphthyl. In some embodiments the bidentate ligand is a dianionic ligand. The dianionic ligand has a net formal oxidation state of -2. In one embodiment, each dianionic ligand independently is carbonate, oxalate (i.e., $^-O_2CC(O)O^-$), (C_2-C_{40})hydrocarbylene dicarbanion, (C_1-C_{40})heterohydrocarbylene dicarbanion, phosphate, or sulfate.

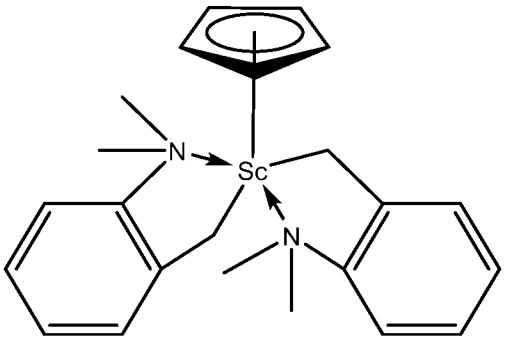
[0189] As previously mentioned, number and charge (neutral, monoanionic, dianionic) of Z1 are selected depending on the formal oxidation state of M such that the metal-ligand complex of Formula (i) is, overall, neutral.

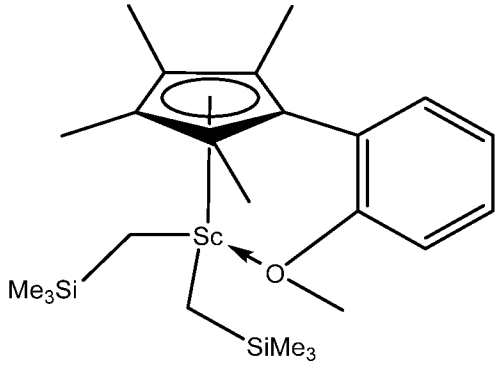
[0190] In some embodiments each Z1 is the same, wherein each Z1 is methyl; isobutyl; neopentyl; neophyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. In some embodiments nn is 2 and each Z1 is the same.

[0191] In some embodiments at least two Z1 are different. In some embodiments, each Z1 is a different one of methyl; isobutyl; neopentyl; neophyl; trimethylsilylmethyl; phenyl; benzyl; and chloro.

[0192] In one embodiment, the metal-ligand complex of Formula (i) is a mononuclear metal complex.

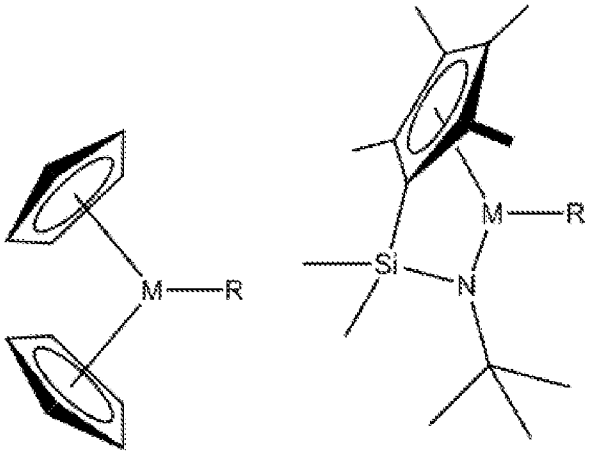
[0193] Further suitable procatalysts include those disclosed in *Acc. Chem. Res.*, **2015**, *48* (8), pp 2209–2220, including but not limited to those of the following structures:





[0194] Suitable procatalyst further include "single-component catalysts" that can catalyze olefin polymerization without the use of a co-catalyst. Such simple-component catalysts include those disclosed in Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337−339; Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53−101; Ihara, E.; Nodono, M.; Katsura, K.; Adachi, Y.; Yasuda, H.; Yamagashira, M.; Hashimoto, H.; Kanehisa, N.; and Kai, Y.*Organometallics* **1998**, *17*, 3945−3956; Long, D. P.; Bianconi, P. A.*J. Am. Chem. Soc.* **1996**, *118*, 12453−12454; Gilchrist, J. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 12021−12028; Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**,*118*, 1045−1053; Evans, W. J.; DeCoster, D. M.; Greaves, J.*Organometallics* **1996**, *15*, 3210−3221; Evans, W. J.; DeCoster, D. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929−7936; Shapiro, P. J.;

Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623–4640; Schaverien, C. J. *Organometallics* **1994**, *13*, 69–82; Coughlin, E. B. *J. Am. Chem. Soc.* **1992**, *114*, 7606–7607; Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406–9407; Burger, B. J.; Thompson, M. E., Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**,*112*, 1566–1577; Shapiro, P. J.; Bunel, E.; Schaefer, W. P.*Organometallics* **1990**, *9*, 867–869; Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103; Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110; and *Organometallics*, **2001**, *20* (9), pp 1752–1761. Exemplary, non-limiting formulas of such simple-component catalysts include:

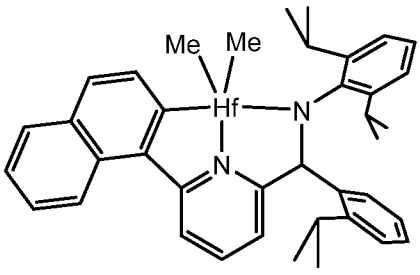


, wherein:

M is Sm or Y; and R is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl.

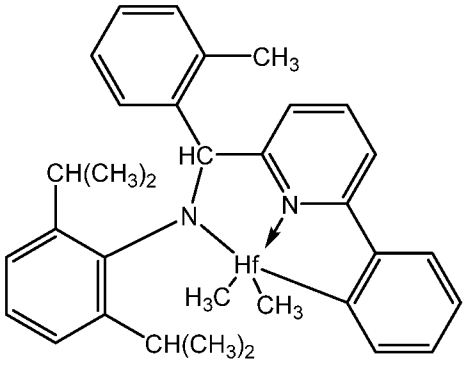
[0195] Suitable procatalysts include but are not limited to the following named as (Cat 1) to (Cat 17).

[0196] (Cat 1) may be prepared according to the teachings of WO 03/40195 and U.S. Patent No. 6,953,764 B2 and has the following structure:



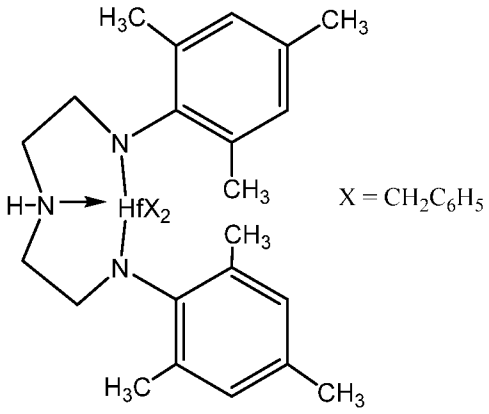
(Cat 1).

[0197] (Cat 2) may be prepared according to the teachings of WO 03/40195 and WO 04/24740 and has the following structure:



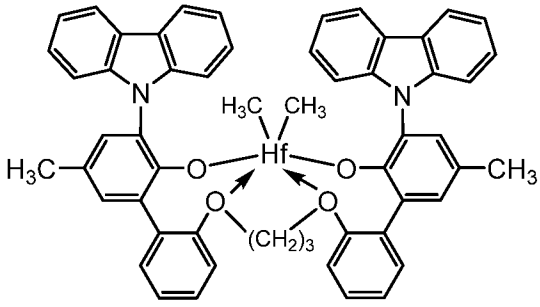
(Cat 2).

[0198] (Cat 3) may be prepared according to methods known in the art and has the following structure:



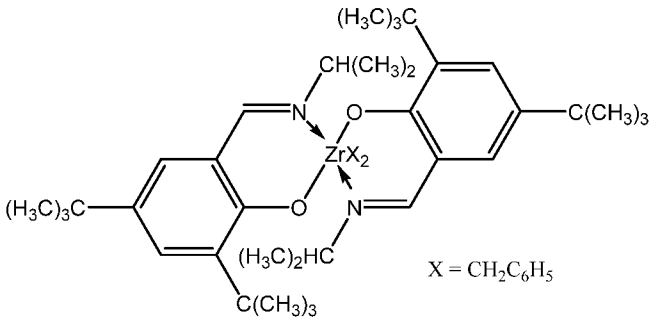
(Cat 3).

[0199] (Cat 4) may be prepared according to the teachings of U.S. Patent Application Publication No. 2004/0010103 and has the following structure:



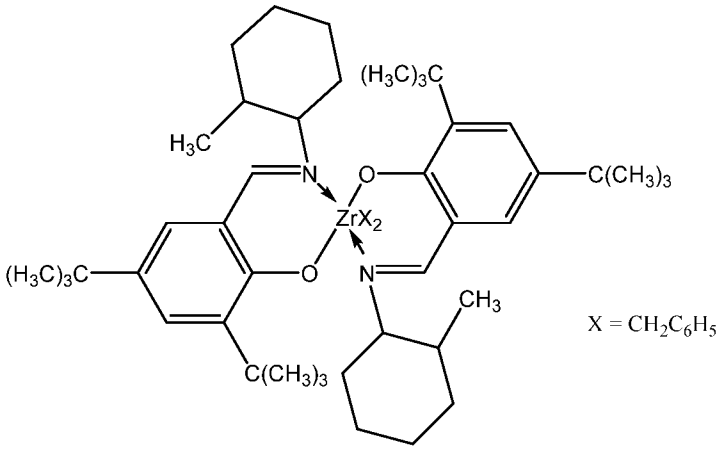
(Cat 4).

[0200] (Cat 5) may be prepared according to the teachings of U.S. Patent No. 7,858,706 B2 and has the following structure:



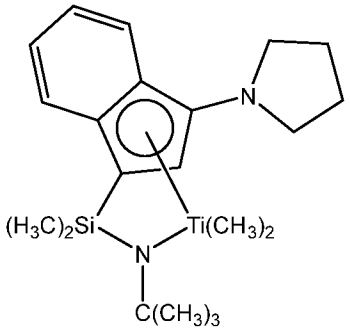
(Cat 5).

[0201] (Cat 6) may be prepared according to the teachings of U.S. Patent No. 7,858,706 B2 and has the following structure:



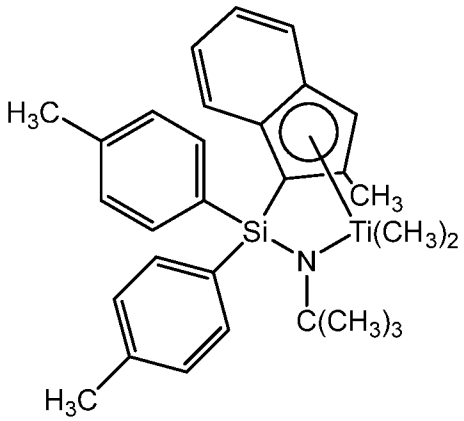
(Cat 6).

[0202] (Cat 7) may be prepared by the teachings of U.S. Pat. No. 6,268,444 and has the following structure:



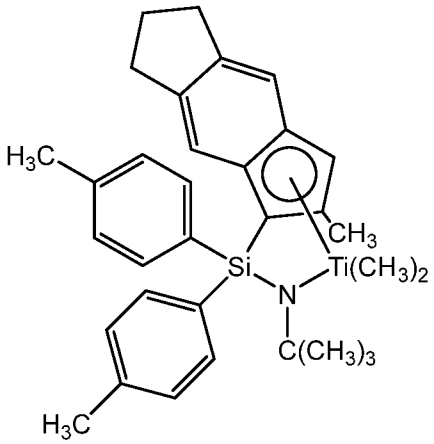
(Cat 7).

[0203] (Cat 8) may be prepared according to the teachings of U.S. Pat. Pub. No. 2003/004286 and has the following structure:



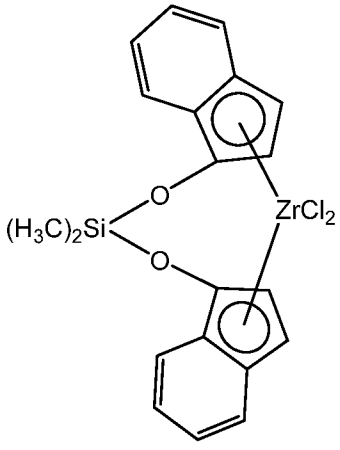
(Cat 8).

[0204] (Cat 9) may be prepared according to the teachings of U.S. Pat. Pub. No. 2003/004286 and has the following structure:



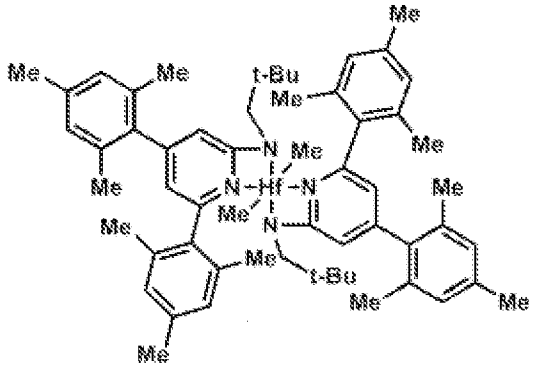
(Cat 9).

[0205] (Cat 10) is commercially available from Sigma-Aldrich and has the following structure:



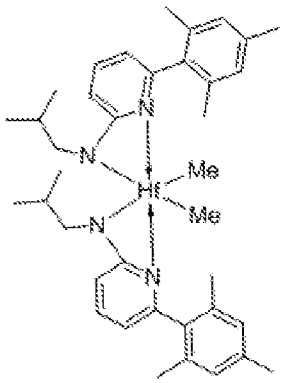
(Cat 10).

[0206] (Cat 11) may be prepared according to the teachings of WO 2017/173080 A1 and has the following structure:



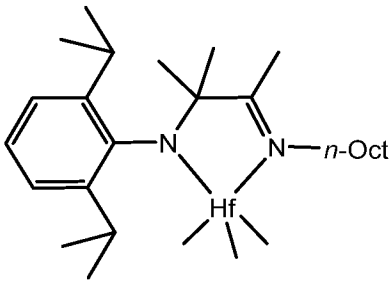
(Cat 11).

[0207] (Cat 12) may be prepared according to the teachings of WO 2017/173080 A1 and has the following structure:



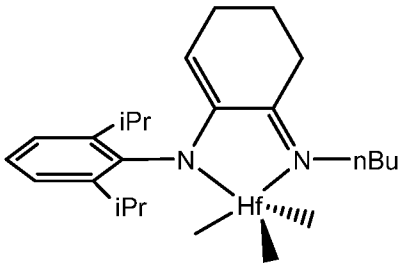
(Cat 12).

[0208] (Cat 13) may be prepared according to the teachings of Macromolecules (Washington, DC, United States), 43(19), 7903-7904 (2010) and has the following structure:



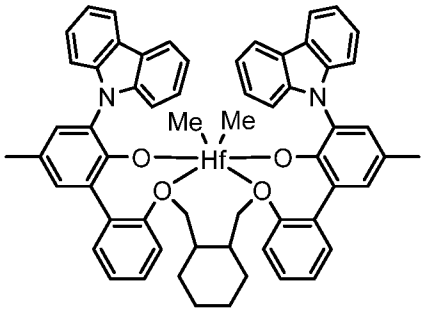
(Cat 13).

[0209] (Cat 14) may be prepared according to the teachings of WO 2011/102989 A1 and has the following structure:



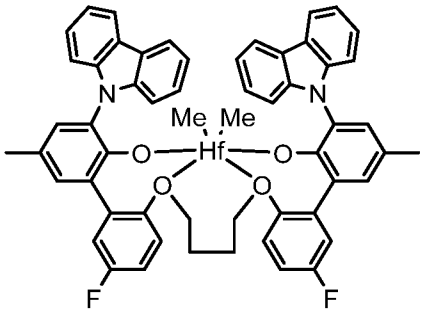
(Cat 14).

[0210] (Cat 15) may be prepared according to the teachings of U.S. Pat. No. 8,101,696 B2 and has the following structure:



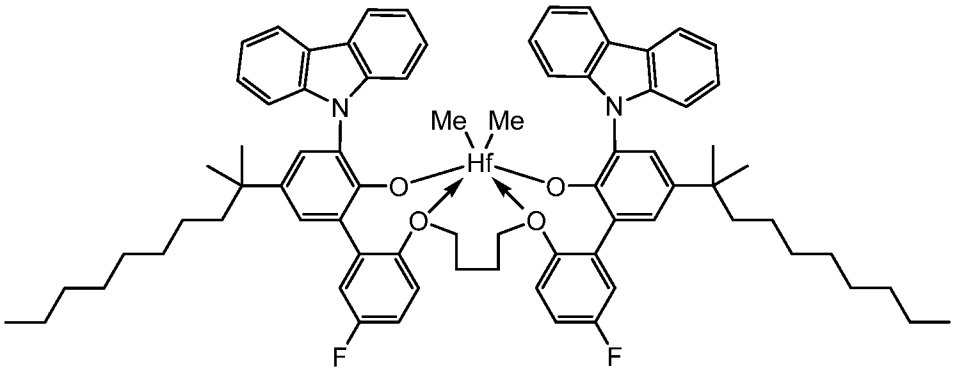
(Cat 15).

[0211] (Cat 16) may be prepared according to the teachings of WO 2018/170138 A1 and has the following structure:



(Cat 16).

[0212] (Cat 17) may be prepared according to the teachings of WO 2018/170138 A1 and has the following structure:



(Cat 17).

[0213] In certain embodiments, the (c1) catalyst component comprises a procatalyst and a co-catalyst. In these embodiments, the procatalyst may be activated to form an active catalyst by combination with a co-catalyst (activator), preferably a cation forming co-catalyst, a strong Lewis acid, or a combination thereof.

[0214] Suitable cation forming co-catalysts include those previously known in the art for metal olefin polymerization complexes. Examples include neutral Lewis acids, such as C_{1-30} hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium-salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating co-catalysts and activating techniques have been previously taught with respect to different metal complexes for olefin polymerizations in the following references: EP-A-277,003; U.S. Pat. Nos. 5,153,157; 5,064,802; 5,321,106; 5,721,185; 5,350,723; 5,425,872; 5,625,087; 5,883,204; 5,919,983; 5,783,512; WO 99/15534, and WO99/42467.

[0215] Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbons in each hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis

acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane may be used as activating cocatalysts. Exemplary molar ratios of metal complex:tris(pentafluorophenyl-borane:alumoxane are from 1:1:1 to 1:5:20, such as from 1:1:1.5 to 1:5:10.

[0216] Suitable ion forming compounds useful as co-catalysts in one embodiment of the present disclosure comprise a cation which is a Brønsted acid capable of donating a proton, and a compatible, noncoordinating anion, A^-. As used herein, the term "noncoordinating" refers to an anion or substance which either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived there from, or which is only weakly coordinated to such complexes thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion which when functioning as a charge balancing anion in a cationic metal complex does not transfer an anionic substituent or fragment thereof to said cation thereby forming neutral complexes. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

[0217] Suitable anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

[0218] In one aspect, suitable cocatalysts may be represented by the following general formula:

$(L^*-H)_g{}^+(A)^{g-}$, wherein:

L* is a neutral Lewis base;

$(L^*-H)^+$ is a conjugate Brønsted acid of L*;

A^{g-} is a noncoordinating, compatible anion having a charge of g–, and g is an integer from 1 to 3.

[0219] More particularly, A^{g-} corresponds to the formula: $[M'Q_4]^-$; wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

Q independently in each occurrence is selected from hydride, dialkyl-amido, halide, hydrocarbyl, hydrocarbyloxide, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo-substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl-perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), each Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxide Q groups are disclosed in U.S. Pat. No. 5,296,433.

[0220] In an exemplary embodiment, g is one, that is, the counter ion has a single negative charge and is A^-. Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this disclosure may be represented by the following general formula: $(L^*–H)^+(BQ_4)^-$; wherein:

L* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl-group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

[0221] Especially useful Lewis base salts are ammonium salts, more preferably trialkyl-ammonium salts containing one or more C_{12-40} alkyl groups. In this aspect, for example, Q in each occurrence can be a fluorinated aryl group, especially, a pentafluorophenyl group.

[0222] Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this disclosure include the tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl)borate,

triethylammonium tetrakis(pentafluorophenyl)borate,

tripropylammonium tetrakis(pentafluorophenyl)borate,

tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,

tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,

N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,

N,N-dimethylanilinium n-butyltris(pentafluorophenyl)borate,

N,N-dimethylanilinium benzyltris(pentafluorophenyl)borate,

N,N-dimethylanilinium tetrakis(4-(t-butyldimethylsilyl)-2,3,5,6 tetrafluorophenyl)borate,

N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2,3,5,6-tetrafluorophenyl)borate,

N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl)borate,

N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,

N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl)borate,

dimethyloctadecylammonium tetrakis(pentafluorophenyl)borate,

methyldioctadecylammonium tetrakis(pentafluorophenyl)borate;

a number of dialkyl ammonium salts such as:

di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,

methyloctadecylammonium tetrakis(pentafluorophenyl)borate,

methyloctadodecylammonium tetrakis(pentafluorophenyl)borate, and

dioctadecylammonium tetrakis(pentafluorophenyl)borate;

various tri-substituted phosphonium salts such as:

triphenylphosphonium tetrakis(pentafluorophenyl)borate,

methyldioctadecylphosphonium tetrakis(pentafluorophenyl)borate, and

tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate;

di-substituted oxonium salts such as:

diphenyloxonium tetrakis(pentafluorophenyl)borate,

di(o-tolyl)oxonium tetrakis(pentafluorophenyl)borate, and

di(octadecyl)oxonium tetrakis(pentafluorophenyl)borate; and

di-substituted sulfonium salts such as:

di(o-tolyl)sulfonium tetrakis(pentafluorophenyl)borate, and

methylcotadecylsulfonium tetrakis(pentafluorophenyl)borate.

[0223] Further to this aspect of the disclosure, examples of useful $(L^*-H)^+$cations include, but are not limited to, methyldioctadecylammonium cations, dimethyloctadecylammonium cations, and ammonium cations derived from mixtures of trialkyl amines containing one or two C_{14-18} alkyl groups.

[0224] Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula: $(Ox^{h+})_g(A^{g-})_h$, wherein:

Ox^{h+} is a cationic oxidizing agent having a charge of h+;

h is an integer from 1 to 3; and

A^{g-} and g are as previously defined.

[0225] Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^{+}, or Pb^{+2}. Particularly useful examples of A^{g-} are those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate.

[0226] Another suitable ion forming, activating cocatalyst can be a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the following formula: $[C]^{+}A^{-}$

wherein:

$[C]^{+}$ is a C_{1-20} carbenium ion; and

is a noncoordinating, compatible anion having a charge of −1. For example, one carbenium ion that works well is the trityl cation, that is triphenylmethylium.

[0227] A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula: $(Q^{1}{}_{3}Si)^{+}A^{-}$

wherein:

Q^{1} is C_{1-10} hydrocarbyl, and A^{-} is as previously defined.

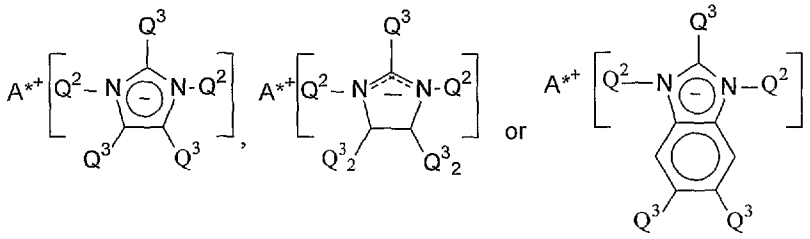
[0228] Suitable silylium salt activating cocatalysts include trimethylsilylium tetrakispentafluorophenylborate, triethylsilylium tetrakispentafluorophenylborate, and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in *J. Chem. Soc. Chem. Comm.* 1993, 383-384, as well as in Lambert, J. B., et al., *Organometallics* 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is also described in U.S. Pat. No. 5,625,087.

[0229] Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present disclosure. Such cocatalysts are disclosed in U.S. Pat. No. 5,296,433.

[0230] Suitable activating cocatalysts for use herein also include polymeric or oligomeric alumoxanes (also called aluminoxanes), especially methylalumoxane (MAO), triisobutyl aluminum modified methylalumoxane (MMAO), or isobutylalumoxane; Lewis acid modified

alumoxanes, especially perhalogenated tri(hydrocarbyl)aluminum- or perhalogenated tri(hydrocarbyl)boron modified alumoxanes, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, and most especially tris(pentafluorophenyl)borane modified alumoxanes. Such co-catalysts are previously disclosed in U.S. Pat. Nos. 6,214,760, 6,160,146, 6,140,521, and 6,696,379.

[0231] A class of co-catalysts comprising non-coordinating anions generically referred to as expanded anions, further disclosed in U.S. Pat. No. 6,395,671, may be suitably employed to activate the metal complexes of the present disclosure for olefin polymerization. Generally, these co-catalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted as follows:



wherein:

A^{*+} is a cation, especially a proton containing cation, and can be trihydrocarbyl ammonium cation containing one or two C_{10-40} alkyl groups, especially a methyldi(C_{14-20} alkyl)ammonium cation,

Q^3, independently in each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including for example mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, such as C_{1-20} alkyl, and

Q^2 is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)alumane).

[0232] Examples of these catalyst activators include trihydrocarbylammonium-salts, especially, methyldi(C_{14-20} alkyl)ammonium-salts of:

bis(tris(pentafluorophenyl)borane)imidazolide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolide,

bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolide,

bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolide,

bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide,
bis(tris(pentafluorophenyl)borane)imidazolinide,
bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide,
bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide,
bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide,
bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide,
bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolide,
bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide,
bis(tris(pentafluorophenyl)alumane)imidazolide,
bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide,
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide,
bis(tris(pentafluorophenyl)alumane)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide,
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide, and
bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.

[0233] Other activators include those described in the PCT publication WO 98/07515, such as tris(2,2′,2″-nonafluorobiphenyl)fluoroaluminate. Combinations of activators are also contemplated by the disclosure, for example, alumoxanes and ionizing activators in combinations, see for example, EP-A-0 573120, PCT publications WO 94/07928 and WO 95/14044, and U.S. Pat. Nos. 5,153,157 and 5,453,410. For example, and in general terms, WO 98/09996 describes activating catalyst compounds with perchlorates, periodates and iodates, including their hydrates. WO 99/18135 describes the use of organoboroaluminum activators. WO 03/10171 discloses catalyst activators that are adducts of Brønsted acids with Lewis acids. Other activators or methods for activating a catalyst compound are described in, for example, U.S. Pat. Nos. 5,849,852, 5,859,653, and 5,869,723, in EP-A-615981, and in PCT publication WO 98/32775. All of the foregoing catalyst activators as well as any other known activator for

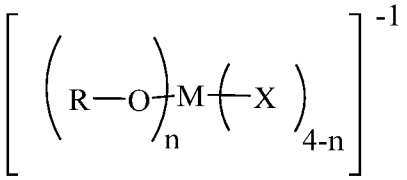
transition metal complex catalysts may be employed alone or in combination according to the present disclosure. In one aspect, however, the co-catalyst can be alumoxane-free. In another aspect, for example, the co-catalyst can be free of any specifically-named activator or class of activators as disclosed herein.

[0234] In a further aspect, the molar ratio of procatalyst/co-catalyst employed generally ranges from 1:10,000 to 100:1, for example, from 1:5000 to 10:1, or from 1:1000 to 1:1. Alumoxane, when used by itself as an activating co-catalyst, can be employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis.

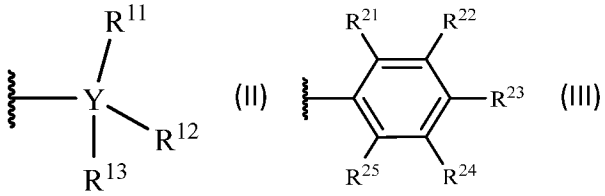
[0235] Tris(pentafluorophenyl)borane, where used as an activating co-catalyst can be employed generally in a molar ratio to the metal complex of from 0.5:1 to 10:1, such as from 1:1 to 6:1 and from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately equimolar quantity with the metal complex.

[0236] In exemplary embodiments of the present disclosure, the co-catalyst is $[(C_{16\text{-}18}H_{33\text{-}37})_2CH_3NH]$ tetrakis(pentafluorophenyl)borate salt.

[0237] Suitable co-catalysts also include those disclosed in U.S. Provisional Pat. App. Nos. 62650423, 62650412, and 62650453, which are incorporated herein by reference in their entirety. Such co-catalysts include those of the ionic complex comprising an anion and a countercation, the anion having the structure:



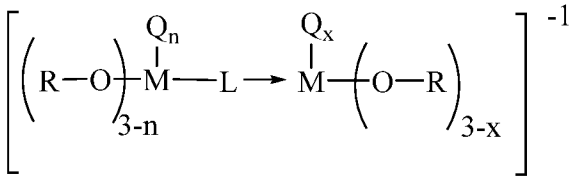
wherein: M is aluminum, boron, or gallium; n is 2, 3, or 4; each R is independently selected from the group consisting of: radical (II) and radical (III):



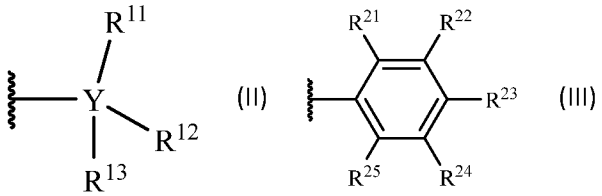
each Y is independently carbon or silicon; each R^{11}, R^{12}, R^{13}, R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} is independently chosen from $(C_1–C_{40})$alkyl, $(C_6–C_{40})$aryl, $–OR^C$, –O–, $–SR^C$, –H, or –F, wherein

when R is a radical according to radical (III), at least one of R^{21-25} is a halogen-substituted (C_1–C_{40})alkyl , a halogen-substituted (C_6–C_{40})aryl, or –F; and provided that: when each R is a radical (II) and Y is carbon, at least one of R^{11-13} is a halogen-substituted (C_1–C_{40})alkyl , a halogen-substituted (C_6–C_{40})aryl, or –F; or when M is aluminum and n is 4 and each R is a radical (II), and each Y is carbon: each R^{11}, R^{12}, and R^{13} of each R is a halogen- substituted (C_1–C_{40})alkyl, a halogen-substituted (C_6–C_{40})aryl, or –F; or a total number of halogen atoms in R^{11}, R^{12}, and R^{13} of each R is at least six; each X is a monodentate ligand independently chosen from halogen-substituted (C_1–C_{20})alkyl, (C_1–C_{20})alkyl, halogen-substituted (C_6–C_{40})aryl, (C_6–C_{40})aryl, triflate, or –$S(O)_3$; optionally, two groups R are covalently connected; each R^N and R^C is independently (C_1–C_{30})hydrocarbyl or –H.

[0238] Such co-catalysts further include the bimetallic activator complex comprising an anion and a countercation, the anion having a structure:

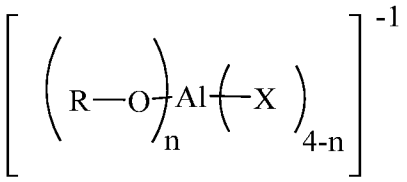


where: each M is independently aluminum, boron, or gallium; L is chosen from a species having at least two Lewis basic sites; each Q is independently a monodentate ligand; n is 0, 1, or 2, wherein when n is 0, Q is not present; x is 0, 1, or 2, wherein when x is 0, Q is not present; each R is independently selected from the group consisting of radical (II) and radical (III):

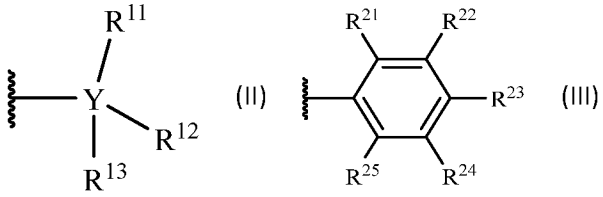


each Y is independently carbon or silicon; each R^{11}, R^{12}, R^{13}, R^{21}, R^{22}, R^{23}, R^{24}, and R^{25}, is independently chosen from (C_1–C_{40})alkyl, (C_6–C_{40})aryl, –H, –NR^N_2, –OR^C, –SR^C, or halogen, wherein when R is radical (II), at least one of R^{11-13} is perhalogenated (C_1–C_{40})alkyl , perhalogenated (C_6–C_{40})aryl, or –F; and when R is radical (III), at least one of R^{21-25} is perhalogenated (C_1–C_{40})alkyl, perhalogenated (C_6–C_{40})aryl, or –F; optionally, when n is 0 or 1, two R groups are covalently connected; and each R^N or R^C is independently (C_1–C_{30})hydrocarbyl or –H.

[0239] Such co-catalysts further include the metallic activator comprising an anion and a countercation, the anion having a structure:



where: n is 0 or 1; each R is independently selected from the group consisting of radical (II) and radical (III):



each Y is independently carbon or silicon; each R^{11}, R^{12}, R^{13}, R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} is independently chosen from (C_1–C_{40})alkyl, halogen-substituted (C_1–C_{40})alkyl, (C_6–C_{40})aryl, halogen-substituted (C_6–C_{40})aryl, $-OR^C$,$-SR^C$, –H, –F or Cl, wherein at least one of R^{11-13} and one of R^{21-25} is a halogen-substituted (C_1–C_{40})alkyl, a halogen-substituted (C_6–C_{40})aryl, or –F; and each X is a monodentate ligand independently chosen from halogen-substituted (C_1–C_{20})alkyl or halogen-substituted (C_6–C_{40})aryl; optionally, two X groups are covalently connected; each R^C is independently halogen-substituted (C_1–C_{30})hydrocarbyl; provided that when the countercation is $(Ph)_3C^+$, and the anion is $Al(C_6F_5)_4$.

(B) Curing Component

[0240] The curable composition further comprises a (B) curing component comprising a crosslinking agent. In certain embodiments, the curable composition of the present disclosure may comprise from 0.01 wt% to 2 wt% (or from 0.05 wt% to 2 wt%, or from 0.1 wt% to 2 wt%, or from 0.1 wt% to 1 wt%, or from 0.1 wt% to 0.6 wt%, or from 0.2 wt% to less than or equal to 0.6 wt%) of the (B) curing component comprising a crosslinking agent, based on the total weight of the curable composition. In further embodiments, the curable composition comprises from 0.1 wt% to less than or equal to 0.6 wt%, or from 0.1 wt% to less than or equal to 0.57 wt%, or from 0.2 wt% to less than or equal to 0.57 wt% of the (B) curing component comprising a crosslinking agent, based on the total weight of the curable composition.

[0241] In certain embodiments, the (B) curing component further comprises co-agents, curing additives, accelerators, and/or scorch inhibitors. In further embodiments, the (B) curing component contains only the crosslinking agent.

[0242] Non-limiting examples of suitable cross-linking agents include peroxides; phenols; azides; aldehyde-amine reaction products; substituted ureas; substituted guanidines; substituted xanthates; substituted dithiocarbamates; sulfur-containing compounds, such as thiazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime, dibenzoparaquinonedioxime, sulfur; imidazoles; silanes; metal oxides, such as zinc, magnesium, and lead oxides; dinitroso compounds, such as p-quinone-dioxime and p,p'-dibenzoylquinone-dioxime; and phenol-formaldehyde resins containing hydroxymethyl or halomethyl functional groups and combinations thereof. The suitability of any of these cross-linking agents will be largely governed by the choice of polymers, as is well known to those skilled in the compounding art.

[0243] The crosslinking agent may include one or more organic peroxides including but not limited to alkyl peroxides, aryl peroxides, peroxyesters, peroxycarbonates, diacylperoxides, peroxyketals, cyclic peroxides, dialkyl peroxides, peroxy esters, peroxy dicarbonates, or combinations of two or more thereof. Examples of peroxides include but are not limited to di-tertbutyl peroxide, dicumyl peroxide, di(3,3,5-trimethyl hexanoyl)peroxide, t-butyl peroxypivalate, t-butyl peroxyneodecanoate, di(sec-butyl)peroxydicarbonate, t-amyl peroxyneodecanoate, 1,1-di-t-butyl peroxy-3,3,5-trimethylcyclohexane, t-butyl-cumyl peroxide, 2,5-dimethyl-2,5-di(tertiary-butyl-peroxyl)hexane, 1,3-bis(tertiary-butyl-peroxyl-isopropyl)benzene, or a combination thereof. An exemplary crosslinking agent is dicumyl peroxide commercially available under the tradename LUPEROX® from Arkema or the tradename TRIGONOX® from Akzo Nobel. A further exemplary crosslinking agent is VAROX® DBPH-50 from Vanderbilt Chemicals. When the cross-linking agent is a peroxide, certain processing aids and cure activators such as stearic acid and ZnO may also be used.

[0244] When peroxide based curing agents are used, co-activators or coagents may be used in combination therewith. Suitable coagents include but are not limited to trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), and 1,4-phenylenedimaleimide (available from TCI Chemicals).

[0245] Suitable coagents further include but are not limited to the alkenyl-functional monocyclic organosiloxanes disclosed in WO 2019/000311 and WO 2019/000654, which are incorporated

herein by reference in their entirety. For example, the coagent may be a monocyclic organosiloxane of the formula [R1,R2SiO2/2]n, wherein subscript n is an integer greater than or equal to 3; each R1 is independently a (C2-C4)alkenyl or a H2C=C(R1a)-C(=O)-O-(CH2)m- wherein R1a is H or methyl and subscript m is an integer from 1 to 4; and each R2 is independently H, (C1-C4)alkyl, phenyl, or R1. Examples of such monocyclic organosiloxanes include but are not limited to 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl cyclotetrasiloxane, 2,4,6-trimethyl-2,4,6-trivinyl-cyclotrisiloxane, or a combination thereof.

[0246] A scorch inhibitor/retardant is a molecule that inhibits premature curing, or a collection of such molecules. Examples of a scorch inhibitor/retardant are hindered phenols; semihindered phenols; TEMPO; TEMPO derivatives; 1,1-diphenylethylene; 2,4-diphenyl-4-methyl-1-pentene (also known as alpha-methyl styrene dimer or AMSD); and allyl-containing compounds described in US 6277925B1, column 2, line 62, to column 3, line 46.

[0247] Suitable cross-linking agents include those that are sulfur based, such as elemental sulfur. When sulfur based curing agents are employed, accelerators and cure activators may be used as well, such as amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates, xanthates, 4,4'-dithiodimorpholine, thiuram di-and polysulfides, alkylphenol disulfides, and 2-morpholino-dithiobenzothiazole, tetramethylthiuram disulfide (TMTD), dipentamethylenethiuram tetrasulfide (DPTT), 2-mercaptobenzothiazole (MBT), 2-mercaptobenzothiazolate disulfide (MBTS), zinc-2-mercaptobenozothiazolate (ZMBT), zinc diethyldithiocarbamatezinc (ZDEC), zinc dibutyldithiocarbamate (ZDBC), dipentamethylenethiuram tetrasulfide (DPTT), N-t-butylbenzothiazole-2-sulfanamide (TBBS), and mixtures thereof.

[0248] Additional crosslinking agents include, but are not limited to, phenolic resins, azides, aldehyde-amine reaction products, vinyl silanes, hydrosilylation agents, substituted ureas, substituted guanidines, substituted xanthates, substituted dithiocarbamates, and combinations thereof. The crosslinking agent may be a phenolic curing agent or a peroxide curing agent, with an optional co-agent, or hydrosilylation cross-linking agent with a hydrosilylation catalyst, or dibutyl tin dilaurate ("DBTDL"), with an optional co-agent alumina trihydrate ("ATH"). Popular industrial catalysts are "Speier's catalyst," H_2PtCl_6, and Karstedt's catalyst, an alkene-stabilized platinum(0) catalyst.

[0249] When a cross-linking agent is used, the cross-linking can be induced by activating the cross-linking agent in the curable formulation. The cross-linking agent can be activated by exposing it to a temperature above its decomposition temperature. Temperatures range from 50°C to 300°C, such as 80°C to 275°C. Time can be determined by one of ordinary skill in the art depending on polymers and cure components selected.

[0250] Alternatively, the cross-linking agent can be activated by exposing it to a radiation that causes the generation of free radicals from the cross-linking agent. Non-limiting examples of suitable radiation include UV or visible radiation, electron beam or beta ray, gamma rays, X-rays, or neutron rays. Radiation is believed to activate the cross-linking by generating radicals in the polymer which may subsequently combine and cross-link. Radiation dosage depends upon many factors and can be determined by those skilled in the art. UV or visible radiation activiation can occur when the cross-linking agent is a peroxide photoinitiator, such as dibenzoyl peroxide, cumene hydroperoxide, di-t-butyl peroxide, diacetyl peroxide, hydrogen peroxide, peroxydisulfates, and 2,2-bis(terbutylperoxy)-2,5-dimethylhexane.

[0251] In some embodiments, dual cure systems, which comprises at least two activation methods, may be effectively employed, such as combinations selected from heat, moisture cure, and radiation. For instance, it may be desirable to employ a peroxide cross-linking agent in conjunction with a silane cross-linking agent, a peroxide cross-linking agent in conjunction with radiation, a sulfur-containing cross-linking agent in conjunction with a silane cross- linking agent, or the like. Those skilled in the art will be readily able to select the amount of cross-linking agent, based on the desired cross-linking level, the characteristics of the polymer such as molecular weight, molecular weight distribution, comonomer content, the presence of cross-linking enhancing coagents, other additives and the like.

[0252] When the (A) polyolefin component is at least partially crosslinked, the degree of crosslinking may be measured by dissolving the composition in a solvent for specified duration, and calculating the percent gel or unextractable component. The percent gel normally increases with increasing crosslinking levels. For cured articles according to the invention, the percent gel content may be from 5 to 100 percent, or from 10 to 95 percent, or from 20 to 90 percent, or from 30 to 85 percent, or from 40 to 80 percent. . In further embodiments, cured articles of the present disclosure may have a gel content from 25 to 100 percent, from 50 to 100 percent, or from 60 to 100 percent.

Applications and End Uses

[0253] The compositions of the present disclosure can be employed in a variety of conventional fabrication processes to produce useful articles, including objects prepared by cast, blown, calendered, or extrusion processes; molded articles, such as blow molded, injection molded, or rotomolded articles; extrusions; fibers; and woven or non-woven fabrics. Compositions of the present disclosure can further include but are not limited to other natural or synthetic polymers, oils, UV stabilizers, pigments, tackifiers, fillers (such as talc, calcium carbonate, glass fiber, carbon fiber), additives, reinforcing agents such as calcium or magnesium carbonate, fatty acids and salts thereof, ignition resistant additives, scorch inhibitors, antioxdiants, stabilizers, colorants, extenders, carbon black, crosslinkers, blowing agents, activators such as zinc oxide or zinc stearate, silica, aluminum silicates, plasticizers such as dialkyl esters of dicarboxylic acids, antidegradants, softeners, waxes, (poly)alcohols, (poly)alcohol ethers, polyesters, metal salts, scavengers, nucleating agents, stability control agents, flame retardants, lubricants, processing aids, extrusion aids, and chemical protectors.

[0254] Fibers may be prepared from the present compositions. Fibers that may be prepared include staple fibers, tow, multicomponent, sheath/core, twisted, and monofilament. Suitable fiber forming processes include spinbonded, melt blown techniques, as disclosed in U.S. Pat. Nos. 4,430,563, 4,663,220, 4,668,566, and 4,322,027, gel spun fibers as disclosed in U.S. Pat. No. 4,413,110, woven and nonwoven fabrics, as disclosed in U.S. Pat. No. 3,485,706, or structures made from such fibers, including blends with other fibers, such as polyester, nylon or cotton, thermoformed articles, extruded shapes, including profile extrusions and co-extrusions, calendared articles, and drawn, twisted, or crimped yarns or fibers. The new polymers described herein are also useful for wire and cable coating operations, as well as in sheet extrusion for vacuum forming operations, and forming molded articles, including the use of injection molding, blow molding process, or rotomolding processes. Compositions can also be formed into fabricated articles such as those previously mentioned using conventional polyolefin processing techniques which are well known to those skilled in the art of polyolefin processing.

[0255] Dispersions (both aqueous and non-aqueous) can also be formed using the present formulations comprising the same.

[0256] Additives and adjuvants may be included in any formulation. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, titanium dioxide, zeolites,

powdered metals, organic or inorganic fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders, including paraffinic or napthelenic oils; and other natural and synthetic polymers, including other polymers according to the invention.

[0257] Suitable polymers for blending as the (D) component include thermoplastic and non-thermoplastic polymers including natural and synthetic polymers. Such polymers include unsaturated polyolefin thermoplastics (EPDM, polybutadiene, etc.), polyolefin thermoplastics with low or no unsaturations (PE, PP, ethylene/alpha-olefin interpolymers), other elastomers (SBCs, PVC, EVA, ionomers, etc.), and other engineering thermoplastics (styrenics, polyamides, polyesters, etc.). Exemplary polymers for blending include polypropylene, (both impact modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of polyethylene, including high pressure, free-radical LDPE, Ziegler Natta LLDPE, metallocene PE, including multiple reactor PE ("in reactor" blends of Ziegler-Natta PE and metallocene PE, such as products disclosed in U.S. Pat. Nos. 6,545,088, 6,538,070, 6,566,446, 5,844,045, 5,869,575, and 6,448,341), etlhylene-vinyl acetate (EVA), ethylene/vinyl alcohol copolymers, polystyrene, impact modified polystyrene, ABS, styrene/butadiene block copolymers and hydrogenated derivatives thereof (SBS and SEBS), ethylene-based olefin block copolymers (such as those available under the trade name INFUSE™ available from the Dow Chemical Company), propylene-based olefin block copolymers (such as those available under the trade name INTUNE™ available from the Dow Chemical Company), and thermoplastic polyurethanes. Homogeneous polymers such as olefin plastomers and elastomers, such as ethylene/alpha-olefin copolymers and propylene-based copolymers with low or no unsaturations (for example polymers available under the trade designation VERSIFY™ available from The Dow Chemical Company, ENGAGE™ from The Dow Chemical Company, TAFMER™ from Mitsui Chemicals, Exact™ from ExxonMobil, and VISTAMAXX™ available from ExxonMobil) can also be useful as components in blends comprising the present polymers.

[0258] Suitable end uses include crosslinkable or non-crosslinkable formulations for films; fibers; soft touch goods, such as tooth brush handles and appliance handles; gaskets and profiles; adhesives (functional adhesives, cross-linked adhesives, hot melt adhesives); footwear (including shoe soles and shoe liners); auto interior parts and profiles; foam goods (both open and closed

cell); impact modifiers for other thermoplastic polymers such as high density polyethylene, isotactic polypropylene, or other olefin polymers; coated fabrics; hoses; tubing; weather stripping; cap liners; flooring; construction or building parts; woodworking; coatings (powder coatings, water-based coatings for beverage and food liners, solvent-based coatings for industrial metal coatings); waterproofing; photovoltaic applications; wire and cable applications; thermoplastic vulcanizates (TPV) applications; EPDM thermosets; seals, belts, conveyor belts, automotive timing belts and the like, gaskets, dampeners; tire compounds; highly filled compounds, sidewall and tread compounds; coagents for thermoset rubbers; crosslinked tubing; liquid (low viscosity) reaction injection molding; injection molded skins; 3D printing; and piping.

[0259] Compositions may also contain anti-ozonants or anti-oxidants that are known to a rubber chemist of ordinary skill. The anti-ozonants may be physical protectants such as waxy materials that come to the surface and protect the part from oxygen or ozone or they may be chemical protectors that react with oxygen or ozone. Suitable chemical protectors include styrenated phenols, butylated octylated phenol, butylated di(dimethylbenzyl) phenol, p-phenylenediamines, butylated reaction products of p-cresol and dicyclopentadiene (DCPD), polyphenolic anitioxidants, hydroquinone derivatives, quinoline, diphenylene antioxidants, thioester antioxidants, and blends thereof. Some representative trade names of such products are Wingstay™ S antioxidant, Polystay™ 100 antioxidant, Polystay™ 100 AZ antioxidant, Polystay™ 200 antioxidant, Wingstay™ L antioxidant, Wingstay™ LHLS antioxidant, Wingstay™ K antioxidant, Wingstay™ 29 antioxidant, Wingstay™ SN-1 antioxidant, and Irganox™ antioxidants. In some applications, the anti-oxidants and anti-ozonants used will preferably be non-staining and non-migratory.

[0260] For providing additional stability against UV radiation, hindered amine light stabilizers (HALS) and UV absorbers may be also used. Suitable examples include Tinuvin™ 123, Tinuvin™ 144, Tinuvin™ 622, Tinuvin™ 765, Tinuvin™ 770, and Tinuvin™ 780, available from Ciba Specialty Chemicals, and Chemisorb™ T944, available from Cytex Plastics, Houston Tex., USA. A Lewis acid may be additionally included with a HALS compound in order to achieve superior surface quality, as disclosed in U.S. Pat. No. 6,051,681.

[0261] For some compositions, additional mixing process may be employed to pre-disperse the anti-oxidants, anti-ozonants, carbon black, UV absorbers, and/or light stabilizers to form a masterbatch, and subsequently to form polymer blends there from.

[0262] Compositions according to the invention may also contain organic or inorganic fillers or other additives such as starch, talc, calcium carbonate, glass fibers, polymeric fibers (including nylon, rayon, cotton, polyester, and polyaramide), metal fibers, flakes or particles, expandable layered silicates, phosphates or carbonates, such as clays, mica, silica, alumina, aluminosilicates or aluminophosphates, carbon whiskers, carbon fibers, nanoparticles including nanotubes, wollastonite, graphite, zeolites, and ceramics, such as silicon carbide, silicon nitride or titanias. Silane based or other coupling agents may also be employed for better filler bonding. Non-limiting examples of suitable silane coupling agents include γ-chloropropyl trimethoxysilane, vinyl trimethoxysilane, vinyl triethoxysilane, vinyl-tris-(β-methoxy)silane, allyltrimethoxysilane, γ-methacryloxypropyl trimethoxysilane, β-(3,4-ethoxy-cyclohexyl)ethyl trimethoxysilane, γ-glycidoxypropyl trimethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-aminopropyl trimethoxysilane, N-β-(aminoethyl)- γ-aminopropyl trimethoxysilane, and 3-(trimethoxysilyl)propylmethacrylate, vinyl triacetoxysilane, γ-(meth)acryloxy, propyl trimethoxysilane, and combinations thereof.

[0263] Suitable blowing agents include but are not limited to inorganic blowing agents, organic blow agents, chemical blowing agents, and combinations thereof. Non-limiting examples of suitable inorganic blowing agents include carbon dioxide, nitrogen, argon, water, air, nitrogen, and helium. Non-limiting examples of suitable organic blowing agents include aliphatic hydrocarbons having 1-6 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Non-limiting examples of suitable aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, and the like. Non-limiting examples of suitable aliphatic alcohols include methanol, ethanol, n- propanol, and isopropanol. Non-limiting examples of suitable fully and partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and chlorofluorocarbons. Non- limiting examples of suitable fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2- tetrafluoro-ethane (HFC- 134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2- difluoropropane, 1,1,1-

trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Non-limiting examples of suitable partially halogenated chlorocarbons and chlorofluorocarbons include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-tricliloroethane, 1,1-dichloro-l-fluoroethane (HCFC- 14 Ib), 1- chloro-1,1 difluoroethane (HCFC-142b), l,l-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-l, 2,2,2 - tetrafluoroethane(HCFC- 124). Non-limiting examples of suitable fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-Il), dichlorodifluoromethane (CFC- 12), trichlorotrifluoroethane (CFC-113), 1,1,1- trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. Non-limiting examples of suitable chemical blowing agents include azodicarbonamide, azodiisobutyro-nitrile, benezenesulfonhydrazide, 4,4-oxybenzene sulfonyl-semicarbazide, p-toluene sulfonyl semi- carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and trihydrazino triazine. In some embodiments, the blowing agent is azodicarbonamide isobutane, CO_2, or a mixture of thereof.

[0264] The (A) polyolefin component of the present disclosure can also be chemically modified, such as by grafting (for example by use of maleic anhydride (MAH), silanes, glycidyl methacrylate, or other grafting agent), halogenation, amination, sulfonation, or other chemical modification.

Specific Embodiments

[0265] The following are non-limiting embodiments that exemplify the present invention and provide detailed disclosures for any claims in this application. Unless stated otherwise, any measured property or characterization in the following embodiments is accordance with the test methods disclosed herein.

1. A curable composition comprising (A) a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP, and (B) a curing component comprising a cross-linking agent, wherein:

L^1 is a polyolefin;

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

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

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

2. A curable composition comprising (A) a polyolefin component comprising a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP and (B) a curing component comprising a cross-linking agent, wherein:

L^1 is a polyolefin;

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

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

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

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

3. A curable composition comprising (A) a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP and a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP and (B) a curing component comprising a cross-linking agent, wherein:

L^1 at each occurrence independently is a polyolefin;

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

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

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

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

4. The curable composition of embodiment 3, wherein the (A) polyolefin component comprises a ratio of the unsaturated polyolefin of the formula A^1L^1 to the telechelic polyolefin of the formula $A^1L^1L^2A^2$ of from 10:90 to 90:10, or from 20:80 to 80:20, or from 40:60 to 60:40, or 50:50.

5. The curable composition of any of the previous embodiments, wherein the curable composition further comprises (C) an additive component and (D) at least one other polymer component comprising an ethylene-based polymer.

6. The curable composition of embodiment 5, wherein the curable composition comprises a ratio of the unsaturated polyolefin of the formula A^1L^1 to the ethylene-based polymer of from 1:99 to 25:75, or from 2:98 to 20:80, or from 4:96 to 11:89.

7. The curable composition of embodiment 5, wherein the curable composition comprises a ratio of the telechelic polyolefin of the formula $A^1L^1L^2A^2$ to the ethylene-based polymer of from 1:99 to 25:75, or from 2:98 to 20:80, or from 4:96 to 11:89.

8. The curable composition of any of embodiments 5-7, wherein the ethylene-based polymer is an ethylene/alpha-olefin copolymer.

9. The curable composition of embodiment 8, wherein the ethylene-based polymer is selected from the group consisting of an ethylene/propylene copolymer, an ethylene/1-butene copolymer, an ethylene/1-hexene copolymer, and an ethylene/1-octene copolymer.

10. The curable composition of any of embodiments 5-7, wherein the ethylene-based polymer is an olefin block copolymer.

11. The curable composition of any of embodiments 5-10, wherein the ethylene-based polymer has a density of from 0.850 to 0.915 g/cc, or from 0.854 to 0.900 g/cc, or from 0.854 to 0.890 g/cc, or from 0.860 to 0.885 g/cc.

12. The curable composition of any of embodiments 5-11, wherein the ethylene-based polymer has a melt index (I2) of from 0.01 to 500 g/10 minutes, or from 0.01 to 100 g/10 minutes, or from 0.5 to 50 g/10 minutes, or from 0.5 to 35 g/10 minutes.

13. The curable composition of any of the previous embodiments, wherein the cross-linking agent is an organic peroxide.

14. The curable composition of any of the previous embodiments, wherein the (B) curing component further comprises a coagent and a silane coupling agent.

15. The curable composition of embodiment 14, wherein the co-agent is selected from the group consisting of triallyl cyanurate (TAC), triallyl phosphate (TAP), triallyl isocyanurate (TAIC), 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl cyclotetrasiloxane, and combinations thereof.

16. The curable composition of embodiments 14-15, wherein the silane coupling agent is selected from the group consisting of vinyl trimethoxysilane (VTMS), 3-(trimethoxysilyl)propylmethacrylate (VMMS), allyltrimethoxysilane, and combinations thereof.

17. The curable composition of embodiments 14-16, wherein the curable composition comprises:

the (A) polyolefin component in an amount of from 1 wt% to 25 wt%, or from 2 wt% to 25 wt%, or from 4 wt% to 25 wt%, or from 1 wt% to 20 wt%, or from 4 wt% to 15 wt%, based on the total weight of the curable composition;

the (B) curing component in an amount of from 0.1 wt% to 15 wt%, or from 0.1 wt% to 10 wt%, or from 0.5 wt% to 5 wt%, based on the total weight of the curable composition; and

the (C) additive component in an amount of from 0 wt% to 2 wt%, or from 0.01 wt% to 1 wt%, or from 0.05 wt% to 0.5 wt%, based on the total weight of the curable composition; and

the (D) other polymer component in an amount of from 50 wt% to 99 wt%, or from 58 wt% to 98 wt%, or from 70 wt% to 97 wt%, or from 80 wt% to 96 wt%, or from 88 wt% to 94 wt%, based on the total weight of the curable composition.

18. The curable composition of embodiments 1-13, wherein the (C) additive component comprises a blowing agent.

19. The curable composition of embodiment 18, wherein the (C) additive component further comprises a blowing agent activator and a filler.

20. The curable composition of embodiment 19, wherein the blowing agent is azodicabonamide or an azodicabonamide-based agent, and the blowing agent activator is zinc oxide, zinc stearate, or a combination thereof.

21. The curable composition of embodiment 19 or 20, wherein the filler is titanium dioxide.

22. The curable composition of embodiments 18-21, wherein the curable composition comprises:

the (A) polyolefin component in an amount of from 1 wt% to 25 wt%, or from 2 wt% to 25 wt%, or from 4 wt% to 25 wt%, or from 1 wt% to 20 wt%, or from 4 wt% to 15 wt%, based on the total weight of the curable composition;

the (B) curing component in an amount of from 0.1 wt% to 2 wt%, or from 0.1 wt% to 1 wt%, or from 0.1 wt% to 0.6 wt%, based on the total weight of the curable composition; and

the (C) additive component in an amount of from 0.5 wt% to 50 wt%, or from 0.5 wt% to 25 wt%, or from 0.5 wt% to 10 wt%, based on the total weight of the curable composition; and

the (D) other polymer component in an amount of from 25 wt% to 99 wt%, or from 40 wt% to 98 wt%, or from 60 wt% to 97 wt%, or from 76 wt% to 96 wt%, or from 85 wt% to 90 wt%, based on the total weight of the curable composition.

23. The curable composition of embodiments 18-22, wherein the (B) curing component comprising the crosslinking agent is present in an amount of from 0.1 wt% to less than or equal

to 0.6 wt% or from 0.1 wt% to less than or equal to 0.57 wt%, based on the total weight of the curable composition.

24. The curable composition of embodiments 18-23, wherein the crosslinking agent is a peroxide, and the crosslinking agent is present in an amount of from 0.1 wt% to less than or equal to 0.6 wt% or from 0.1 wt% to less than or equal to 0.57 wt%, based on the total weight of the curable composition.

25. The curable composition of any of the previous embodiments,

wherein each L^1 independently is an ethylene homopolymer comprising units derived from ethylene,

wherein each A^1 independently is a vinyl group, a vinylene group of the formula $Y^1CH=CH–$, or a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, and

wherein each Y^1 independently is a methyl group.

26. The curable composition of any of embodiments 1-24,

wherein each L^1 indepedently is a propylene homopolymer comprising units derived from propylene,

wherein each A^1 indepedently is a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, or a mixture of a vinylidene group of the formula $CH_2=C(Y^1)–$ and a vinylene group of the formula $Y^1CH=CH–$, and

wherein Y^1 at each occurrence independently is a methyl group.

27. The curable composition of any of embodiments 1-24, wherein each L^1 independently is an ethylene/alpha-olefin copolymer comprising units derived from ethylene and a C_3 to C_{30} alpha-olefin, and wherein the C_3 to C_{30} alpha-olefin is selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene.

28. The curable composition of embodiment 27, wherein the C_3 to C_{30} alpha-olefin is propylene and each L^1 independently is an ethylene/propylene copolymer; and

wherein each A^1 independently is a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, or a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, and

wherein Y^1 at each occurrence independently is a methyl group.

29. The curable composition of embodiment 27, wherein the C_3 to C_{30} alpha-olefin is 1-butene and each L^1 indepedently is an ethylene/1-butene copolymer,

wherein each A^1 independently is a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, or a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, and

wherein Y^1 at each occurrence independently is an ethyl group.

30. The curable composition of embodiment 27, wherein the C_3 to C_{30} alpha-olefin is 1-hexene and each L^1 independently is an ethylene/1-hexene copolymer,

wherein each A^1 independently is a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, or a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, and

wherein Y^1 at each occurrence independently is a butyl group.

31. The curable composition of embodiment 27, wherein the C_3 to C_{30} alpha-olefin is 1-octene and each L^1 independently is an ethylene/1-octene copolymer,

wherein each A^1 independently is a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of

the formula $CH_2=C(Y^1)–$, or a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, and

wherein Y^1 at each occurrence independently is a C6 alkyl group.

32. The curable composition of any of embodiments 1-24, wherein each L^1 independently is a propylene/alpha-olefin copolymer comprising units derived from propylene and either ethylene or a C_4 to C_{30} alpha-olefin, wherein the C_4 to C_{30} alpha-olefin is selected from the group consisting of 1-butene, 1-hexene, and 1-octene.

33. The curable composition of embodiment 32, wherein each L^1 independently is a propylene/ethylene copolymer, and

wherein each A^1 independently is a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylene group of the formula $Y^1CH=CH–$, a mixture of a vinyl group and a vinylidene group of the formula $CH_2=C(Y^1)–$, or a mixture of a vinyl group, a vinylidene group of the formula $CH_2=C(Y^1)–$, and a vinylene group of the formula $Y^1CH=CH–$, and

wherein Y^1 at each occurrence independently is a methyl group.

34. The curable composition of any of embodiment 2-33, wherein L^2 is $–CH_2CH(Y^2)–$, and wherein Y^2 is hydrogen or a C_1 to C_{30} hydrocarbyl group.

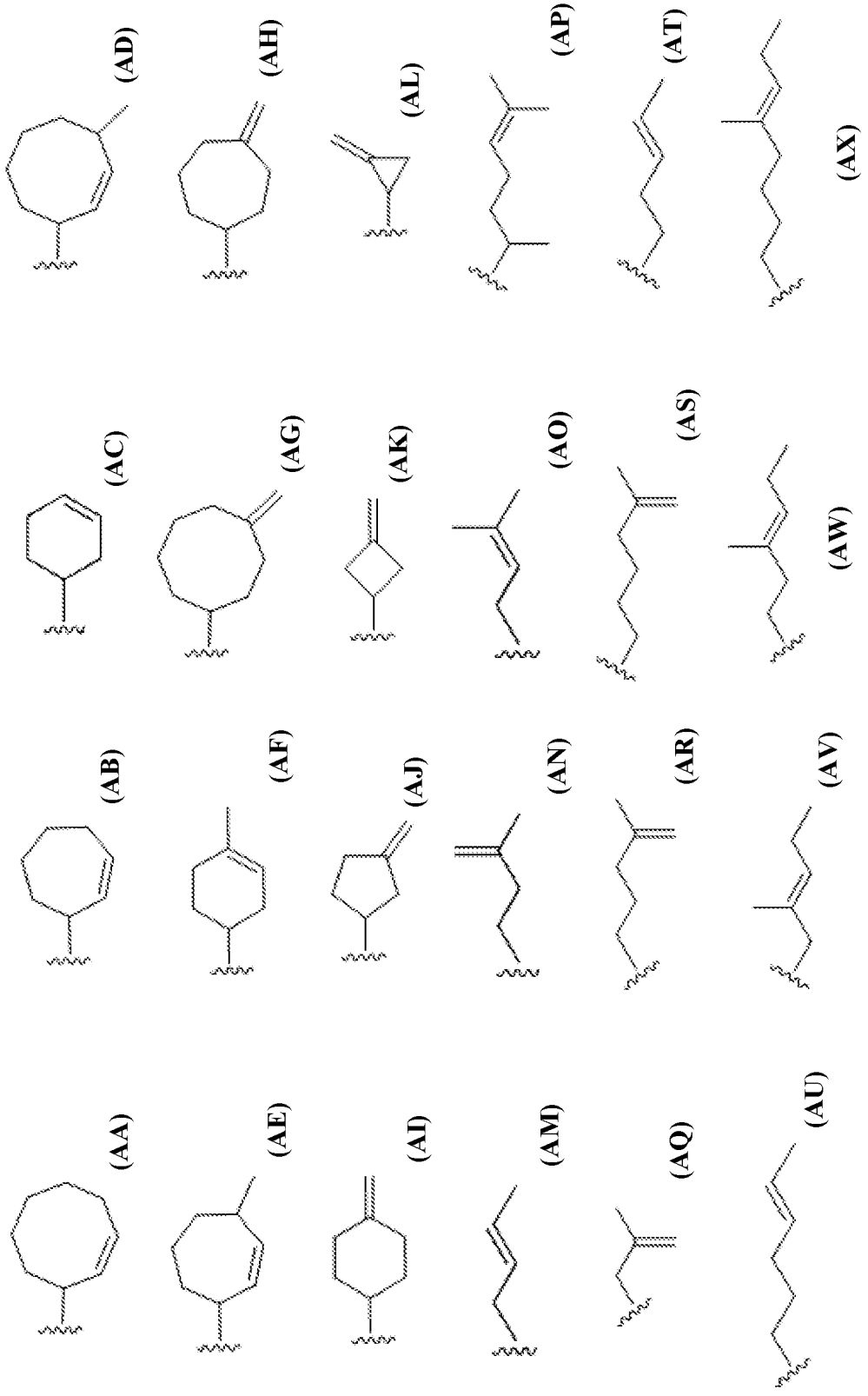
35. The curable composition of embodiment 34, wherein Y^2 is hydrogen or a C1 to C10 alkyl group.

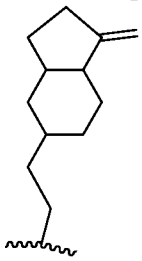
36. The curable composition of any embodiments 2-35, wherein the hindered double bond is selected from the group consisting of the double bond of a vinylidene group, the double bond of a vinylene group, the double bond of a trisubstituted alkene, and the double bond of a vinyl group attached to a branched alpha carbon.

37. The curable composition of any of embodiments 2-36, wherein each A^2 independently is a C_3 to C_{30} cyclic hydrocarbyl group or a C_3 to C_{30} acyclic hydrocarbyl group.

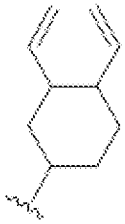
38. The curable composition of any of embodiments 2-37, wherein each A^2 independently is selected from the group consisting of an unsubstituted cycloalkene, an alkyl-substituted cycloalkene, and an acyclic alkyl group.

39. The curable composition of any of embodiments 2-38, wherein each A^2 independently is selected from the group consisting of:


(AA)
(AB)
(AC)
(AD)
(AE)
(AF)
(AG)
(AH)
(AI)
(AJ)
(AK)
(AL)
(AM)
(AN)
(AO)
(AP)
(AQ)
(AR)
(AS)
(AT)
(AU)
(AV)
(AW)
(AX)



(AZ1).



(AZ).



(AY)

40. The curable composition of any of embodiments 2-39, wherein each A^2 independently is selected from the group consisting of (AC), (AF), (AM), (AO), (AP), (AS), and (AZ1).

41. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a weight average molecular weight (Mw) of from 1,000 to 40,000 g/mol, or from 1,000 to 35,000 g/mol, or from 1,000 to 30,000 g/mol, or from 1,000 to 25,000 g/mol.

42. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a number average molecular weight (Mn) of from 1,000 to 18,000 g/mol, or from 1,000 to 16,000 g/mol, or from 1,000 to 14,000 g/mol, or from 1,000 to 12,000 g/mol, or from 1,000 to 10,000 g/mol.

43. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has an average molar mass (Mz) of from 1,000 to 125,000 g/mol, or from 1,000 to 100,000 g/mol, or from 1,000 to 75,000 g/mol, or from 1,000 to 60,000 g/mol, or from 10,000 to 50,000 g/mol.

44. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has an Mw/Mn (PDI) of from 1 to 10, or from 1 to 7, or from 1 to 5, or from 1.5 to 4, and or from 2 to 4.

45. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a density of from 0.850 to 0.965 g/cc, or from 0.854 to 0.950 g/cc, or from 0.854 to 0.935 g/cc, or from 0.854 to 0.925 g/cc, or from 0.854 to 0.910 g/cc, or from 0.854 to 0.900 g/cc, or from 0.854 to 0.885 g/cc, or from 0.854 to 0.880 g/cc, or from 0.854 to 0.875 g/cc.

46. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a melt index (I2) of from 50 to 2,000 g/10 minutes, or from 100 to 2,000 g/10 minutes, or from 200 to 1,500 g/10 minutes or from 300 to 1,500 g/10 minutes, or from 400 to 1,100 g/10min.

47. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a T_m of from -25 °C to 165 °C, or from -25 °C to 150 °C, or from -25 °C to 125 °C, or from -25 °C to 100 °C, or from 0 °C to 80 °C, or from 10 °C to 60 °C.

48. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a Brookfield viscosity (at 177 °C) from 10 to 100,000 cP, or from 50 to 100,000 cP, or from 500 to 100,000 cP, or from 1,000 to 50,000 cP, or from 1,000 cP to 40,000 cP, or from 5,000 cP to 15,000 cP.

49. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has an enthalpy of melting (ΔHm) of from 0 to 235 J/g, or from 0 to 200 J/g, or from 10 to 175 J/g, or from 10 to 150 J/g, or from 10 to 125 J/g, or from 20 to 117 J/g.

50. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ has a T_g of from -80 to 100 °C, or from -80 to 75 °C, or from -80 to 50 °C, or from -80 to 25 °C, or from -80 to 0 °C, or from -80 to -15 °C, or from -70 to -30 °C.

51. The curable composition of any of the previous embodiments, wherein each of the unsaturated polyolefin of the formula A^1L^1 and the telechelic polyolefin of the formula $A^1L^1L^2A^2$ comprises from 0 wt% to 0.001 wt% of units derived from diene monomers.

52. The curable composition of any of embodiments 2-51, wherein the telechelic polyolefin of the formula $A^1L^1L^2A^2$ comprises a total number of unsaturations of from equal to or greater than 1.1, or from equal to or greater than 1.2, or from equal to or greater than 1.3, or from equal to or greater than 1.4, or from equal to or greater than 1.5, or from equal to or greater than 1.6, or rom equal to or greater than 1.7, or from equal to or greater than 1.8, or from equal to or greater than 1.9.

53. The curable composition of any of embodiments 1 and 3-51, wherein the unsaturated polyolefin of the formula A^1L^1 comprises a total number of unsaturations of equal to or greater than 0.6, or equal to or greater than 0.7, or equal to or greater than 0.8, or equal to or greater than 0.9, or equal to or greater than 1.0, or equal to or greater than 1.1, or equal to or greater than 1.2, or equal to or greater than 1.3.

54. The curable composition of embodiments 1-13 and 18-53, wherein the curable composition has an MH-ML of greater than or equal to 3.0 dNm, or greater than or equal to 3.1 dNm, or greater than or equal to 3.2 dNm after curing at 180°C for 15 minutes.

55. The curable composition embodiments 1-13 and 18-54, wherein the curable composition has an MH-ML from greater than or equal to 3.0 dNm to less than or equal to 20 dNm, or from greater than or equal to 3.0 dNm to less than or equal to 15 dNm, or from greater than or equal to 3.0 dNm to less than or equal to 10 dNm, of from greater than or equal to 3.0 dNm to less than or equal to 5 dNm, or from greater than or equal to 3.0 dNm to less than or equal to 4.2 dNm after curing at 180°C for 15 minutes.

56. The curable composition of embodiments 1-13 and 18-55, wherein the curable composition has a viscosity (at 100 rad/s and 130 °C) from less than or equal to 2800 Pa-s, or from less than or equal to 2600 Pa-s, or from less than or equal to 2400 Pa-s, or from less than or equal to 2200 Pa-s, or from less than or equal to 2000 Pa-s before curing.

57. The curable composition embodiments 1-13 and 18-56, wherein the curable composition has a viscosity (at 100 rad/s and 130 °C) from greater than or equal to 500 Pa-s to less than or equal to 2800 Pa-s, or from greater than or equal to 1000 Pa-s to less than or equal to 2800 Pa-s, or from greater than or equal to 1500 Pa-s to less than or equal to 2800 Pa-s, of from greater than or equal to 2000 Pa-s to less than or equal to 2800 Pa-s before curing.

58. An article made from the curable composition of any of embodiments 1-13, 18-57, 78, and 79.

59. The article of embodiment 58, wherein the article is a crosslinked foam.

60. The article of embodiment 58 or 59, wherein the article is a footwear article.

61. The article of any of embodiments 58-60, wherein the article has an expansion ratio from 100% to 200%, or from 130% to 170%, or from 145% to 155%.

62. The article of any of embodiments 58-61, wherein the article has, in accordance with ASTM D624, a Type C tear of greater than or equal to 10.0 N/mm, or greater than or equal to 10.5 N/mm, or greater than or equal to 11.0 N/mm, or greater than or equal to 11.5 N/mm, or greater than or equal to 12.1 N/mm.

63. The article of any of embodiments 58-62, wherein the article has, in accordance with ASTM D624, a Type C tear of from greater than or equal to 10.0 N/mm to less than or equal to 30 N/mm, or from greater than or equal to 10.0 N/mm to less than or equal to 25 N/mm, or from greater than or equal to 10.0 N/mm to less than or equal to 20 N/mm, or from greater than or equal to 10.0 N/mm to less than or equal to 15 N/mm, or from greater than or equal to 10.0 N/mm to less than or equal to 12.5 N/mm.

64. The article of any of embodiments 58-63, wherein the article has, in accordance with the method described herein, a shrinkage of less than or equal to 1.6%, or less than or equal to 1.4%, or less than or equal to 1.3%, or less than or equal to 1.2%, or less than or equal to 1.1%.

65. The article of any of embodiments 58-64, wherein the article has, in accordance with the method described herein, a shrinkage of from greater than or equal to 0.1% to less than or equal to 1.6%, or from greater than or equal to 0.4% to less than or equal to 1.6%, or from greater than or equal to 0.8% to less than or equal to 1.6%, or from greater than or equal to 1.0% to less than or equal to 1.6%.

66. The article of any of embodiments 58-65, wherein the article has, in accordance with the method described herein, a rebound of greater than or equal to 60%, or greater than or equal to 65%, or greater than or equal to 67%, or greater than or equal to 68%.

67. The article of any of embodiments 58-66, wherein the article has, in accordance with the method described herein, a rebound of from greater than or equal to 60% to less than or equal to 90%, or from greater than or equal to 60% to less than or equal to 85%, or from greater than or equal to 60% to less than or equal to 80%, or from greater than or equal to 65% to less than or equal to 75%, or from greater than or equal to 65% to less than or equal to 70%.

68. The article of any of embodiments 58-67, wherein the article has, in accordance with the method described herein, an Asker C hardness of greater than or equal to 40, or greater than or equal to 45, or greater than or equal to 50, or greater than or equal to 54, or greater than or equal to 58.

69. The article of any of embodiments 58-68, wherein the article has, in accordance with the method described herein, an Asker C hardness of from greater than or equal to 50 to less than or equal to 80, or from greater than or equal to 50 to less than or equal to 75, or from greater than or equal to 50 to less than or equal to 70, or from greater than or equal to 50 to less than or equal to 65, or from greater than or equal to 50 to less than or equal to 60.

70. The curable composition of embodiments 1-17 and 25-53, wherein the curable composition has an MH-ML of greater than or equal to 2.6 dNm, or greater than or equal to 2.8

dNm, or greater than or equal to 3.0 dNm, or greater than or equal to 3.2 dNm after curing at 150°C for 25 minutes.

71. The curable composition of embodiments 1-17, 25-53, and 70, wherein the curable composition has an MH-ML from greater than or equal to 2.6 dNm to less than or equal to 20 dNm, or from greater than or equal to 2.6 dNm to less than or equal to 15 dNm, or from greater than or equal to 2.6 dNm to less than or equal to 10 dNm, of from greater than or equal to 2.6 dNm to less than or equal to 7 dNm, or from greater than or equal to 3.0 dNm to less than or equal to 5.3 dNm after curing at 150°C for 25 minutes.

72. The curable composition of embodiments 1-17, 25-53, and 70-71, wherein the curable composition has a viscosity (at 100 rad/s and 110 °C) from less than or equal to 1100 Pa-s, or from less than or equal to 1000 Pa-s, or from less than or equal to 900 Pa-s, or from less than or equal to 880 Pa-s, or from less than or equal to 800 Pa-s before curing.

73. The curable composition of embodiments 1-17, 25-53, and 70-72, wherein the curable composition has a viscosity (at 100 rad/s and 110 °C) from greater than or equal to 500 Pa-s to less than or equal to 1100 Pa-s, or from greater than or equal to 600 Pa-s to less than or equal to 1100 Pa-s, or from greater than or equal to 700 Pa-s to less than or equal to 1100 Pa-s, of from greater than or equal to 900 Pa-s to less than or equal to 1100 Pa-s, or from greater than or equal to 600 Pas to less than or equal to 850 Pa-s before curing.

74. The curable composition of embodiments 1-17, 25-53, and 70-73, wherein the curable composition has a film lamination gel content of greater than or equal to 60%, or greater than or equal to 70%, or greater than or equal to 80% after film lamination at 150 °C for 16 minutes.

75. An article made from the curable composition of any of embodiments 1-17, 25-53, 70-74, 78, and 79.

76. The article of embodiment 75, wherein the article is an encapsulant film.

77. A PV module comprising the encapsulant film of embodiment 76.

78. The curable composition of any of embodiments 1, 3-57, and 70-74, wherein L^1 of the unsaturated polyolefin of the formula A^1L^1 is covalently bonded to A^1 through a carbon-carbon single bond.

79. The curable composition of any of embodiments 2-57, 70-74 and 78, wherein L^1 of the telechelic polyolefin of the formula $A^1L^1L^2A^2$ is covalently bonded to each of A^1 and L^2 through carbon-carbon single bonds, and wherein L^2 of the telechelic polyolefin of the formula $A^1L^1L^2A^2$ is covalently bonded to A^2 through a carbon-carbon single bond.

Testing Methods

[0266] Unless stated otherwise, the measurable properties discussed in the foregoing disclosure and the examples that follow are in accordance with the following analytical methods.

Density

[0267] Samples that were measured for density were prepared according to ASTM D-1928, which is incorporated herein by reference in its entirety. Measurements were made within one hour of sample pressing using ASTM D-792, Method B, which is incorporated herein by reference in its entirety.

Melt Index/Melt Flow Rate

[0268] Melt index (I_2) was measured in accordance with ASTM D-1238, which is incorporated herein by reference in its entirety, Condition 190 °C/2.16 kg, and was reported in grams eluted per 10 minutes. Melt flow rate (I_{10}) was measured in accordance with ASTM D-1238, Condition 190 °C/10 kg, and was reported in grams eluted per 10 minutes.

GPC

[0269] Sample polymers were tested for their properties via GPC according to the following.

[0270] A high temperature Gel Permeation Chromatography system (GPC IR) consisting of an Infra-red concentration detector (IR-5) from PolymerChar Inc (Valencia, Spain) was used for Molecular Weight (MW) and Molecular Weight Distribution (MWD) determination. The carrier

solvent was 1,2,4-trichlorobenzene (TCB). The auto-sampler compartment was operated at 160 °C, and the column compartment was operated at 150 °C. The columns used were four Polymer Laboratories Mixed A LS, 20 micron columns. The chromatographic solvent (TCB) and the sample preparation solvent were from the same solvent source with 250 ppm of butylated hydroxytoluene (BHT) and nitrogen sparged. The samples were prepared at a concentration of 2 mg/mL in TCB. Polymer samples were gently shaken at 160 °C for 2 hours. The injection volume was 200 µl, and the flow rate was 1.0 ml/minute.

[0271] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards. The molecular weights of the standards ranged from 580 to 8,400,000 g/mol, and were arranged in 6 "cocktail" mixtures, with at least a decade of separation between individual molecular weights.

[0272] The GPC column set was calibrated before running the examples by running twenty-one narrow molecular weight distribution polystyrene standards. The molecular weight (Mw) of the standards ranges from 580 to 8,400,000 grams per mole (g/mol), and the standards were contained in 6 "cocktail" mixtures. Each standard mixture had at least a decade of separation between individual molecular weights. The standard mixtures were purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards were prepared at 0.025 g in 50 mL of solvent for molecular weights equal to or greater than 1,000,000 g/mol and 0.05 g in 50 mL of solvent for molecular weights less than 1,000,000 g/mol. The polystyrene standards were dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures were run first and in order of decreasing highest molecular weight (Mw) component to minimize degradation. The polystyrene standard peak molecular weights were converted to polyethylene Mw using the Mark-Houwink constants. Upon obtaining the constants, the two values were used to construct two linear reference conventional calibrations for polyethylene molecular weight and polyethylene intrinsic viscosity as a function of elution column.

[0273] The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

$$M_{polyethylene}=A(M_{polystyrene})^{B} \qquad (1)$$

[0274] Here B has a value of 1.0, and the experimentally determined value of A is around 0.41.

[0275] A third order polynomial was used to fit the respective polyethylene-equivalent calibration points obtained from equation (1) to their observed elution volumes of polystyrene standards.

[0276] Number, weight, and z-average molecular weights were calculated according to the following equations:

$$\overline{Mn} = \frac{\sum^i Wf_i}{\sum^i \left({Wf_i}/{M_i}\right)} \quad (2) \qquad \overline{Mw} = \frac{\sum^i (Wf_i * M_i)}{\sum^i Wf_i} \quad (3)$$

$$\overline{Mz} = \frac{\sum^i (Wf_i * M_i^2)}{\sum^i (Wf_i * M_i)} \quad (4)$$

[0277] Where, Wf_i is the weight fraction of the i-th component and M_i is the molecular weight of the i-th component.

[0278] The MWD was expressed as the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn).

[0279] The accurate A value was determined by adjusting A value in equation (1) until Mw calculated using equation (3) and the corresponding retention volume polynomial, agreed with the known Mw value of 120,000 g/mol of a standard linear polyethylene homopolymer reference.

[0280] The GPC system consists of a Waters (Milford, Mass.) 150 °C high temperature chromatograph (other suitable high temperatures GPC instruments include Polymer Laboratories (Shropshire, UK) Model 210 and Model 220) equipped with an on-board differential refractometer (RI). Additional detectors could include an IR4 infra-red detector from Polymer ChAR (Valencia, Spain), Precision Detectors (Amherst, Mass.) 2-angle laser light scattering detector Model 2040, and a Viscotek (Houston, Tex.) 150R 4-capillary solution viscometer. A GPC with the last two independent detectors and at least one of the first detectors is sometimes referred to as "3D-GPC", while the term "GPC" alone generally refers to conventional GPC. Depending on the sample, either the 15-degree angle or the 90-degree angle of the light scattering detector was used for calculation purposes.

[0281] Data collection was performed using Viscotek TriSEC software, Version 3, and a 4-channel Viscotek Data Manager DM400. The system was equipped with an on-line solvent degassing device from Polymer Laboratories (Shropshire, UK). Suitable high temperature GPC columns could be used, such as four 30 cm long Shodex HT803 13 micron columns or four 30 cm Polymer Labs columns of 20-micron mixed-pore-size packing (MixA LS, Polymer Labs).

The sample carousel compartment was operated at 140 °C and the column compartment was operated at 150 °C. The samples were prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contain 200 ppm of butylated hydroxytoluene (BHT). Both solvents were sparged with nitrogen. The polyethylene samples were gently stirred at 160 °C for four hours (4 h). The injection volume was 200 microliters (μL). The flow rate through the GPC was set at 1 mL/minute.

NMR (^{13}C and ^{1}H)

[0282] Sample Preparation: For ^{13}C NMR, a sample was prepared by adding approximately 2.7 g of stock solvent to 0.20-0.40 g of sample in a 10 mm NMR tube. The stock solvent is tetrachlorethane-d_2 containing 0.025M chromium acetylacetonate (relaxation agent). The samples were capped and sealed with Teflon tape. The samples were dissolved and homogenized by heating the tube and its contents at 135-140°C.

[0283] Sample Preparation: For ^{1}H NMR, a sample was prepared by adding 130 mg of sample to 3.25 g of 50/50 by weight tetrachlorethane-d_2/Perchloroethylene with 0.001 M $Cr(AcAc)_3$ in a 10 mm NMR tube. The samples were purged by bubbling N_2 through the solvent via a pipette inserted into the tube for approximately 5 minutes to prevent oxidation, capped, sealed with Teflon tape. The samples were heated and vortexed at 115°C to ensure homogeneity.

[0284] Data Acquisition Parameters: For ^{13}C NMR, the data was collected using a Bruker 400/600 MHz spectrometer equipped with a Bruker high-temperature CryoProbe (see Reference 1 noted below). The data was acquired using 256-8000 transients per data file, a 7.3 sec pulse repetition delay (6 sec delay + 1.3 sec acq. time), 90 degree flip angles, and a modified inverse gated decoupling with a sample temperature of 120°C (see Reference 2 noted below). All measurements were made on non-spinning samples in locked mode. Samples were homogenized immediately prior to insertion into the heated (125°C) NMR Sample changer, and were allowed to thermally equilibrate in the probe for 7 minutes prior to data acquisition.

[0285] Data Acquisition Parameters: ^{1}H NMR was performed on a Bruker AVANCE 400/600 MHz spectrometer equipped with a Bruker high-temperature CryoProbe and a sample temperature of 120°C. Two experiments were run to obtain spectra, a control spectrum to quantify the total polymer protons, and a double presaturation experiment, which suppresses the intense polymer backbone peaks and enables high sensitivity spectra for quantitation of the end-groups. The control was run with ZG pulse, 4 scans, SWH 10,000 Hz, AQ 1.64s, D_1 14s. The

double presaturation experiment was run with a modified pulse sequence, lc1prf2.zz1, TD 32768, 100 scans, DS 4, SWH 10,000 Hz, AQ 1.64s, D_1 1s, D_{13} 13s.

[0286] Data Analysis: The comonomer content was analyzed with corresponding matrix or algebra method. The unsaturation was analyzed with the method in Reference 3 noted below.

[0287] Reference 1: Z. Zhou, R. Kuemmerle, J. C. Stevens, D. Redwine, Y. He, X. Qiu, R. Cong, J. Klosin, N. Montañez, G. Roof, Journal of Magnetic Resonance, 2009, 200, 328.

[0288] Reference 2: Z. Zhou, R. Kümmerle, X. Qiu, D. Redwine, R. Cong, A. Taha, D. Baugh, B. Winniford, Journal of Magnetic Resonance: 187 (2007) 225.

[0289] Reference 3: Z. Zhou, R. Cong, Y. He, M. Paradkar, M. Demirors, M. Cheatham, W. deGroot, Macromolecular Symposia, 2012, 312, 88.

Brookfield Viscosity

[0290] The Brookfield viscosity was measured at 177 °C in accordance with ASTM D-3236, using a Brookfield RV-DV-II-Pro viscometer and spindle SC-31.

GC/MS

[0291] 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 at 50 °C for 0.5 min
then 25 °C/min to 200 °C, and hold for 5 min
Run Time 11 min

DSC

[0292] Differential Scanning Calorimetry (DSC) was performed using a TA Instruments Discovery DSC, equipped with an RCS cooling unit and an autosampler. A nitrogen purge gas flow of 50 mL/min was used. The higher molecular weight samples (< 50 dg/min melt index at 190 °C) were pressed into a thin film, at 190°C, on a Carver Hydraulic press, at a pressure of 20,000 psi, and for a time of 4 minutes, followed by cooling at a temperature of 23 °C, at a

pressure of 20,000 psi for a time of 1 minute. About 3 – 10 mg of material was cut from the pressed film, weighed, placed in a light aluminum pan, and crimped shut. For the low molecular weight samples (> 50 dg/min melt index at 190 °C), about 3 – 10 mg of material was cut from the as-received bale, weighed, placed in a light aluminum pan, and crimped shut. The thermal behavior of the samples was investigated using the following temperature profile: the sample was rapidly heated to 180°C, and held isothermally for 5 minutes. The sample was then cooled to -90°C, at 10°C/min, and held isothermally for 5 minutes. The sample was then heated to 150°C at 10°C/min. The cooling and second heating curves were used for analysis. The glass transition temperature (Tg), melting temperature (Tm), and heat of enthalpy (ΔHm) were obtained from the second heat data. The crystallization temperature (Tc) was obtained from the first cool data. The Tg was determined using the half-height method. The Tm and Tc were determined as the peak of the melting endotherm and crystallization exotherm, respectively. The percent crystallinity is calculated by dividing the heat of fusion (Hf), determined from the second heat curve, by a theoretical heat of fusion of 292 J/g for PE, and multiplying this quantity by 100 (for example, % cryst. = (Hf / 292 J/g) x 100 (for PE)). If the example contains majority propylene, the theoretical heat of fusion of 165 J/g for PP is used.

DMS

[0293] Rheology was measured on an Advanced Rheometric Expansion System (ARES), equipped with "25 mm" stainless steel parallel plates. Constant temperature dynamic frequency sweeps, in the frequency range of 0.1 to 100 rad/s, were performed under nitrogen purge at 190°C. Samples approximately "25.4 mm in diameter" and "3.2 mm thick" were compression molded on a Carver hydraulic hot press at a temperature of 190°C, at a pressure of 20,000 psi, for a time of four minutes, followed by cooling at a temperature of 23°C, at a pressure of 20,000 psi, for a time of one minute. The sample was placed on the lower plate, and allowed to melt for five minutes. The plates were then closed to a gap of 2.0 mm, and the sample trimmed to "25 mm in diameter." The sample was allowed to equilibrate at 190°C for five minutes, before starting the test. The complex viscosity was measured at constant strain amplitude of 10%. Viscosity at 0.1 rad/s (V0.1) and at 100 rad/s (V100) are reported, along with the ratio (V0.1/V100) of the two viscosity values.

[0294] For polyolefin resins, samples were molded and tested at 190 °C with a strain amplitude of 10%. For curable foam formulations, rheology was measured before crosslinking, with

molding and testing at 130 °C and strain amplitude of 7%. For curable PV encapsulant formulations, rheology was measured before crosslinking, with molding and testing at 110 °C and strain amplitude of 5%.

Moving Die Rheometer

[0295] The cure kinetic profiles (also known as curing curves) of each formulation were measured using an MDR-2000 instrument. For curable foam formulations, a 4 gram sample of the formulation was cut from the roll milled blanket (described below) and was placed between two pieces of polyester Melinex S films. The test was carried out at 180°C over a period of 15 minutes at a frequency of 1.67 Hz and 7% strain. The rheology or curve of torque as a function of time for each formulated composition was measured from samples of uncured blanket, which was then cured during the analysis. For curable PV encapsulant formulations, the MDR was loaded with 5 g of the pellet sample after soaking. The sample was placed between two pieces of polyester Melinex S films. The MDR was run for 25 min to produce a time vs torque curve at 1.67 Hz, 7% strain, and 150 °C, which represented module lamination temperature. The visco-elastic properties, such as minimum S' torque (ML) and maximum S' torque (MH) were measured during the cure cycle. The change in torque, MH-ML, was then calculated for each sample.

Film Lamination Gel Content

[0296] The cured plaque prepared from the film lamination process is cut into small pieces, 3 mm x 3 mm. Then about 0.5 g sample is weighed (Ws) and then sealed in a metal mesh (mesh number is 120) and weight of the packed sample is measured (Wt1). The packed sample is put into a 500 mL flask equipped with condenser and containing 350 mL xylene. After refluxing in xylene for 5 h, the packed samples are removed from xylene, put into a vacuum oven and heated to 120 °C for 2 h under vacuum condition. The packed sample is removed from the vacuum oven and weighed (Wt2). The gel content is calculated as: Film Lamination Gel content = (Wt2 – Wt1)/Ws*100.

Mechanical Properties

Type C Tear

[0297] Bun foam skin layers were submitted for ASTM D624 (Tear, Type C) mechanical property test at 20 inches/minute. The sample thickness was approximately 3 mm.

Falling Ball Rebound

[0298] A 5/8" diameter steel ball was dropped from a height of 500 mm onto the bun foam skin and foam layers to determine the %Rebound. The %Rebound is calculated as rebound height (in mm)*100 /500.

Asker C Hardness

[0299] Asker C Hardness was measured on the bun foam with skin using an Asker C durometer and a 5 s hold time. An average of five readings taken acorss the surface of the sample is reported.

Oven Shrinkage Test

[0300] After skin layers (top and bottom) were removed from the bun foams, samples were cut using the vertical band saw. The mass, thickness, length, and width dimensions are measured. Then the sample is placed in a pre-heated oven at 70 °C for 40 minutes. Samples dimensions were re-measured after 24 hours of cooling at room temperature. The average change in length and width of the foam sample were used to calculate the percent shrinkage of the foam.

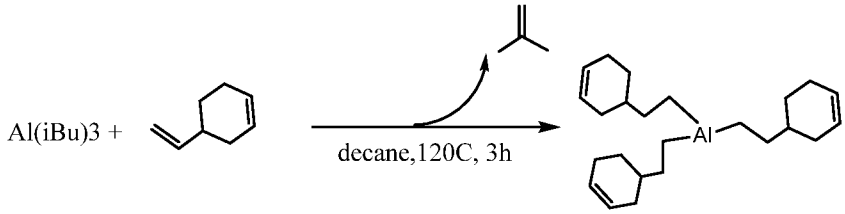
EXAMPLES

Preparation of Chain Transfer Agents (CTA's)

[0301] Unless otherwise noted, all starting reagents and materials were obtained from Sigma-Aldrich. The procatalysts (Cat 1), (Cat 13), (Cat 14), and (Cat 17), as well as any others, used in the examples below are the same as those discussed previously and prepared according to the methods discussed previously. Procatalyst (Cat 1) may also be identified as [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl. "Cocat A" is the co-catalyst used in the examples below and is bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl) borate(1-) amine.

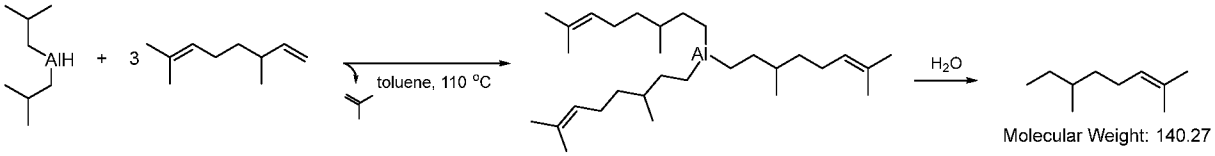
[0302] Synthesis of tris(2-(cyclohex-3-en-1-yl)ethyl)aluminum ("CTA 1"). An exemplary chain transfer agent of the present disclosure was prepared as follows. In a drybox, 4-vinyl-1-cyclohexene (3.2 mL, 24.6 mmol) and triisobutylaluminum (2.0 ml, 7.92 mmol) were added to 5

mL of decane in a vial equipped with a stirbar and a venting needle on the cap. This mixture was heated at 120° C with stirring for 3 hours. After 3 hours, a sample was dissolved in benzene-d6 for ^{1}H NMR analysis, and another aliquot was hydrolyzed with water and analyzed by GC/MS. ^{1}H NMR showed all vinyl groups reacted and the internal double bond remained (FIG. 1A). GC/MS showed a clean peak at m/z of 110, consistent to the molecular weight of ethylcyclohexene (FIG. 1B). Accordingly, ^{1}H NMR and GC/MS confirmed the synthesis of tris(2-(cyclohex-3-en-1-yl)ethyl)aluminum ("CTA 1") via non-limiting Scheme 1.



Scheme 1.

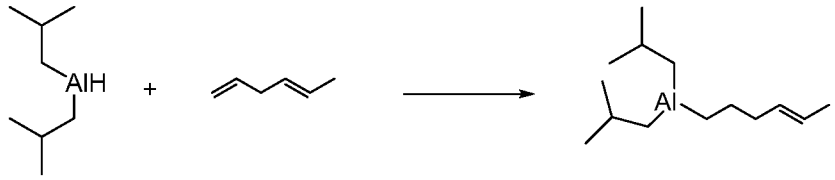
[0303] Synthesis of tris(3,7-dimethyloct-6-en-1-yl)aluminum ("CTA 2"): In a nitrogen-filled drybox, a 40 mL vial was equipped with a stirbar and charged with DIBAL-H (8.10 mL, 9.64 mmol; 20 wt% solution in toluene) and citronellene (4.00 g, 28.93 mmol; mixture of isomers). The vial was placed in a heating block and a vent needle was inserted into the headspace. The solution was heated at 110 – 112 °C for 9 hours giving a colorless transparent solution ([Al] = 0.88 M). The material was determined to be the desired product via ^{1}H NMR (FIG. 2) of an aliquot dissolved in C_6D_6 as well as the GC/MS of a hydrolyzed aliquot (m/z = 140). Accordingly, ^{1}H NMR and GC/MS confirmed the synthesis of tris(3,7-dimethyloct-6-en-1-yl)aluminum ("CTA 2") via non-limiting Scheme 2.



Scheme 2.

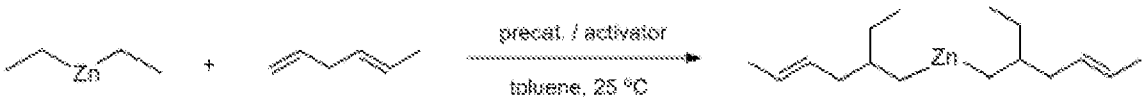
[0304] Synthesis of hex-4-en-1-yldiisobutylaluminum ("CTA 3"): An exemplary chain transfer agent of the present disclosure was prepared as follows. In a nitrogen-filled drybox, DIBAL-H (0.800 g, 5.63 mmol) and 1,4-hexadiene (0.65 mL, 5.63 mmol, d 0.710; mixture of *cis* and *trans* isomers) were added to 3 mL of dry, degassed toluene. The reaction mixture was stirred at 25 °C for 14 hours. ^{1}H NMR analysis of a hydrolyzed sample (see hydrolysis procedure below) showed no reaction. The solution was heated at 60 °C with stirring for 22 hours. After the vial

was allowed to cool to 25 °C an aliquot was hydrolyzed and analyzed. Complete reaction was observed by ^{1}H NMR indicated by the disappearance of the starting diene and appearance of signals consistent with the hydrolysis products: isobutane and 2-hexene. Hydrolysis for analysis was carried out by diluting ca 0.1 mL of the sample to ca 2 mL with C_6D_6 in a vial, removing the sample from the glove box, and adding ca 0.1 mL of nitrogen-purged water via syringe. After shaking the vial the mixture was passed through a 0.45 μm syringe filter. The organic phase passes through more easily than the aqueous phase, allowing for quick isolation of the organic phase for analysis. The sample was then mixed with a small amount of silica gel and filtered again. This helps remove residual Al species that can cause gelation. Accordingly, ^{1}H NMR confirmed the synthesis of hex-4-en-1-yldiisobutylaluminum ("CTA 3") via non-limiting Scheme 3.



Scheme 3.

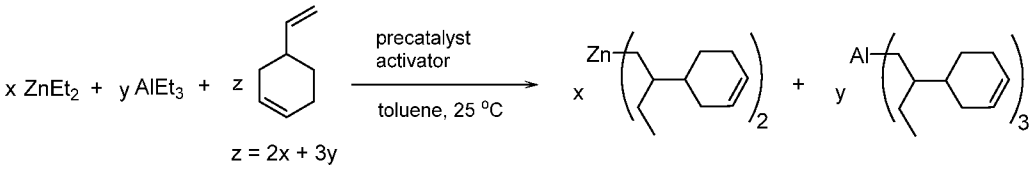
[0305] Synthesis of bis(-2-ethylhex-4-en-1-yl)zinc ("CTA 4"): In a nitrogen-filled drybox, diethylzinc (3.40 mL, 5.00 mmol, 20 wt% in toluene), 1,4-hexadiene (1.16 mL, 10.00 mmol, d 0.710; mixture of *cis* and *trans* isomers), and the activator $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$ (1.40 mL, 0.09 mmol, 0.064 M in methylcyclohexane) were mixed in a vial. (Cat 13) (0.045 g, 0.08 mmol)) was added as a solid and the reaction mixture was stirred at 25 °C for 20 hours. ^{1}H NMR and GC/MS analysis of a hydrolyzed sample (see hydrolysis procedure below) showed complete reaction. ^{1}H NMR indicated by the disappearance of the starting diene and appearance of signals consistent with the hydrolysis product 5-methylhept-2-ene. GC/MS showed the same expected hydrolysis product. Accordingly, ^{1}H NMR and GC/MS confirmed the synthesis of bis(-2-ethylhex-4-en-1-yl)zinc ("CTA 4") via non-limiting Scheme 4.



Scheme 4.

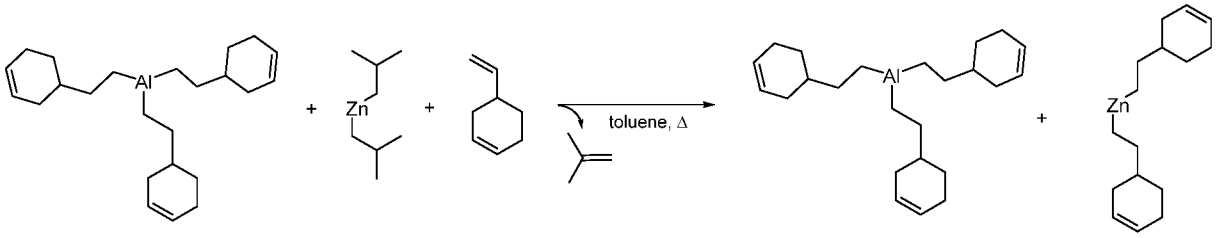
[0306] Synthesis of "CTA 5": Diethylzinc (0.66 mL, 0.97 mmol; 1.47 M solution in toluene), 4-vinylcyclohexene (1.77 mL, 13.58 mmol; d 0.832), the activator ($[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$)

solution in methylcyclohexane (0.60 mL, 0.039 mmol; 0.0644M) and triethylaluminum (0.53 mL, 3.88 mmol; neat, 93%) were dissolved in toluene (~10 mL). (Cat 13) (0.023 g, 0.039 mmol) was added as a solid and the reaction mixture was stirred at 25 °C for 14 hours. An aliquot was dissolved in C_6D_6 and quenched with water. GC/MS and ^{1}H NMR confirmed the consumption of 4-vinylcyclohexene and the formation of the desired product (m/z = 138). Accordingly, this confirms that CTA 5 was prepared via non-limiting Scheme 5.



Scheme 5.

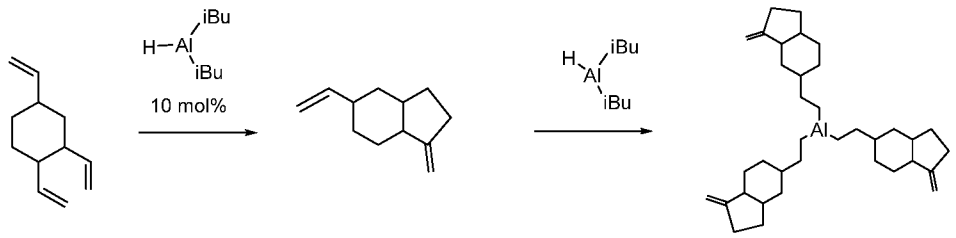
[0307] Synthesis of "CTA 6": The toluene solution of tris(2-(cyclohex-3-en-1-yl)ethyl)aluminum (10 mL, [Al] = 0.424 M) was mixed with diisobutylzinc (0.286 g, 1.59 mmol) and 4-vinylcyclohexene (0.416 mL, 3.19 mmol; d 0.830). The solution was heated for 4 hours at 110 °C with a vent needle inserted through the septum cap of the vial to allow isobutylene to escape. During this treatment ^{i}Bu groups from DIBZ transferred to Al and thermal elimination of isobutylene followed by 4-vinylcyclohexene insertions ensured that all alkyl groups on Al and Zn were cyclohexenylethyl groups. An aliquot (0.1 mL) of this mixture was diluted with C_6D_6 (0.5 mL) and hydrolyzed for ^{1}H NMR analysis. ^{1}H NMR analysis confirmed CTA was synthesized via non-limiting Scheme 6.



Scheme 6.

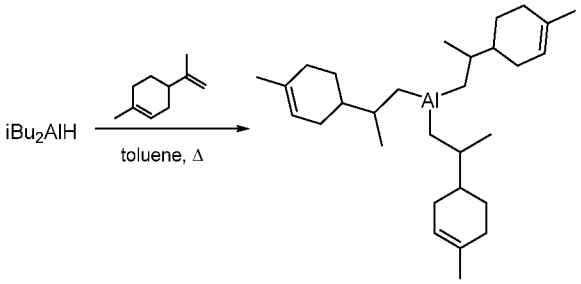
[0308] Synthesis of "CTA 7": The synthesis of CTA 7 is exemplified in non-limiting Scheme 7 and described as follows. It was carried out in two steps. In the first step, trivinylcyclohexane (TVCH) was converted to a diene via intramolecular cyclization in the presence of catalytic amount of DIBAL-H, and in the second step additional DIBAL-H was added to form the CTA. Thus, in a nitrogen-filled drybox, DIBAL-H (0.30 g, 2.11 mmol) was added to TVCH (4.09 mL, 21.1 mmol; d 0.836). The mixture was heated at 160 °C and stirred for 2h to form cyclized-

TVCH. In a separate vial additional DIBAL-H (0.35 g, 2.46 mmol) was dissolved in decane (5 mL), followed by addition of a portion of the cyclized-TVCH (2.05 mL, 10.5 mmol) obtained above. The solution was maintained at 130 °C for 2 h to obtain the Al-TVCH solution.



Scheme 7.

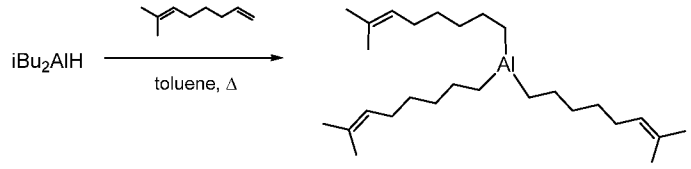
[0309] Synthesis of "CTA 8": The synthesis of CTA 8 is exemplified in non-limiting Scheme 8 and described as follows. In a nitrogen-filled drybox, a 20 mL vial was equipped with a stirbar and charged with DIBAL-H (2.00 mL, 2.39 mmol; 20 wt% in toluene (1.196 M)) and (R)-(+)-limonene (2.32 mL, 14.35 mmol; d 0.842). The vial was placed in a heating block, a vent needle was inserted through the septum cap, and the solution was heated at 110 – 112 °C for 11 hours. Solvent and excess limonene were removed under vacuum at 50 °C overnight to afford the desired product as a colorless viscous oil (0.870 g, 83%).



Scheme 8.

[0310] Synthesis of "CTA 9": The synthesis of CTA 9 is exemplified in non-limiting Scheme 9 and described as follows. In a nitrogen-filled drybox a 40 mL vial was equipped with a stirbar and charged with DIBAL-H (2.00 g, 14.06 mmol), toluene (9.2 mL) and 7-methyl-1,6-octadiene (5.24 g, 42.19 mmol). An immediate exotherm (with some bubbling) was observed. The vial was placed in a heating block, a vent needle was inserted through the septum cap, and the solution was heated at 110 – 112 °C for 3 hours. After 3 hours of reaction time an aliquot showed reaction progress. The solution contained a small amount of suspended white solid particles. The reaction was continued for another 22 hours. The reaction was nearly complete.

A small amount of dimer formation from the alkene reagent was observed. The reaction was continued for another 16 hours. Analysis of an aliquot showed no significant changes.



Scheme 9.

Batch Reactor Synthesis of Telechelic Polyolefins

[0311] Three sets of non-limiting examples of the telechelic polyolefin of the formula $A^1L^1L^2A^2$ were synthesized via batch reactor as follows.

Set 1

[0312] With reference to Tables 1A-1C, Set 1 includes inventive telechelic polymers made in runs BR1 to BR12 that were prepared as follows. In each run, a one gallon stirred autoclave reactor is charged with Isopar™ E mixed alkanes solvent (~1.3 kg), desired mass of propylene, or octene, and/or ethylidene norbornene (ENB) (60 g) and CTA. The reactor is heated to 120° C and charged with ethylene (20 g). An active catalyst solution is prepared in a drybox under inert atmosphere by mixing procatalyst and an activator mixture (a mixture of 1.2 equiv of Cocat A and 10 equiv of modified methyl aluminoxane (MMAO-3A)), where the active catalyst solution has a ratio of procatalyst to Cocat A of 1:1.2. The active catalyst solution is injected into the reactor to initiate the polymerization. The reactor pressure and temperature is kept constant by feeding ethylene during the polymerization and cooling the reactor as needed. After 10 minutes, the reactor was heated to 200 °C and kept at the temperature for 20 minutes. The ethylene feed is shut off and the polymer solution transferred into a nitrogen-purged resin kettle. An additive solution containing a phosphorus stabilizer and phenolic antioxidant (Irgafos® 168 and Irganox® 1010 in a 2:1 ratio by weight in toluene) is added to give a total additive content of approximately 0.1% in the polymer. The polymer is thoroughly dried in a vacuum oven. .

Table 1A

Run	CTA 1 (mmol)	Ethylene (g)	Propylene (g)	Step 1		Step 2		Yield (g)	Efficiency (g-Pol/g-M)	Mn, g/mol	Mw, g/mol	Mw/ Mn
				Temp. (°C)	Time (min)	Temp. (°C)	Time (min)					
BRA	0	22	61	120	10	200	20	35.2	9,860	143,003	727,981	5.1
BR1	0.66	20	62	120	10	200	20	54.7	15,323	29,864	109,316	3.7
BR2	1.33	19	62	120	10	200	20	60.5	16,948	19,729	61,983	3.1
BR3	2	19	61	120	10	200	20	32.6	9,132	14,129	44,304	3.1
BR4	2.66	18	62	120	10	200	20	27.8	7,788	8,840	35,203	4.0

Table 1B

Run		BR5	BR6	BR7	BR8	BR9	BR10	BR11	BRB	BR12
Catalyst		Cat 1	Cat 17	Cat 1	Cat 17	Cat 1	Cat 1	Cat 17	Cat A*	Cat A*
Catalyst (mmol)		0.03	0.0003	0.0065	0.031	0.035	0.0175	0.015	0.0006	0.0019
CTA		CTA 1	CTA 1	CTA 1	CTA 1	CTA 1	CTA 1	CTA 1	--	CTA1
CTA (mmol)		10	0.68	10	6.3	10	10	0.68	0	6.3
Ethylene (g)		0	5.4	5.1	4	2.3	5.7	1.9	30.6	29
Propylene (g)		100	202	301	150	--	--	--	102	101
Octene (g)		--	--	--	--	30	21	30	--	--
ENB (mL)		--	--	--	--	--	--	--	4.4	4.4
Step 1	Temp. (°C)	120	130	120	120	120	120	120	120	120
Step 1	Time (min)	10	10	10	10	10	10	10	10	10
Step 2	Temp. (°C)	200	200	200	200	200	200	200	--	200
Step 2	Time (min)	20	20	20	20	20	20	20	--	20
Yield (g)		10.6	34.3	69.5	36.5	36.7	53.4	50.6	11.2	31.4
Efficiency (g-Pol/g-M)		1,985	642,322	60,069	6,615	5,891	17,143	18,951	205,128	181,608

*Cat A = Zirconium,[2,2’’’-[1,3-propanediylbis(oxy-κO)bis[3’’,5,5’’-tris(1,1-dimethylethyl)-5’-methyl[1,1’:3’,1’’-terphenyl]-2’-olato-κO]]dimethyl-, (OC-6-33)-

Table 1C

Run		BR5	BR6	BR7	BR8	BR9	BR10	BR11	BRB	BR12

Mn (g/mol)		2,759	193,481	7,495	136,766	1,134	1,613	52,297	48,589	63,408
Mw (g/mol)		6,714	524,693	26,840	282,774	2,270	5,474	159,337	95,524	147,907
Mw/Mn		2.43	2.71	3.58	2.07	2.00	3.39	3.05	1.97	2.33
13C NMR	C2 mol%	--	26.3	35.8	30.9	73.3	90.5	83.3	82.9	81.7
13C NMR	C3 mol%	100.0	73.7	64.2	69.1	--	--	--	16.4	17.4
13C NMR	C8 mol%	--	--	--	--	26.7	9.5	16.7	--	--
13C NMR	ENB mol%	--	--	--	--	--	--	--	0.7	0.9
1H NMR	#Vinyls/ 1000000C	28	40	551	62	5190	4806	139	35	152
1H NMR	#Vinylidenes/ 1000000C	2695	33	937	52	1971	800	23	31	66
1H NMR	#Vinylenes/ 1000000C	215	20	6	0	423	169	47	21	93
1H NMR	#Cyclohexenes/ 1000000C	1853	10	1093	98	6767	5313	168	--	200
1H NMR	#Trisubstituted alkenes/1000000C (including ENB)	0	3	0	0	47	32	4	4578	4119
1H NMR	#Unsaturations/ 1000C	4.791	0.106	2.587	0.212	14.398	11.120	0.381	4.665	4.630
Calculation	Unsats/chain	1.42	2.00	1.83	2.79	2.10	1.65	2.14	17.92 0.33**	23.41 1.57**

**Excluding ENB

Set 2

[0313] With reference to Table 2, Set 2 includes inventive telechelic polymers made in runs B1-B7 via a similar procedure as Set 1. Run B1 used the scavenger MMAO-3A with a (Cat 1):Cocat A:scavenger ratio of 1:1.2:10. Runs B2 to B7 used a procatalyst to cocatalyst ratio of 1:1.2. All runs in Table 2 were carried out without hydrogen. All runs had the following conditions: Ethylene (g): 20, 1-octene (g): 60, pressure (psi): 55, solvent (Isopar E, g): 1325. CTA 5 loading was based on the number of transferrable groups. Runs B1, B2, B4 and B6 were at 120 °C for 10 min. Runs B3, B5 and B7 included an additional heating step at 200 °C for 20 min (excluding the transition time from 120 to 200 °C).

Table 2

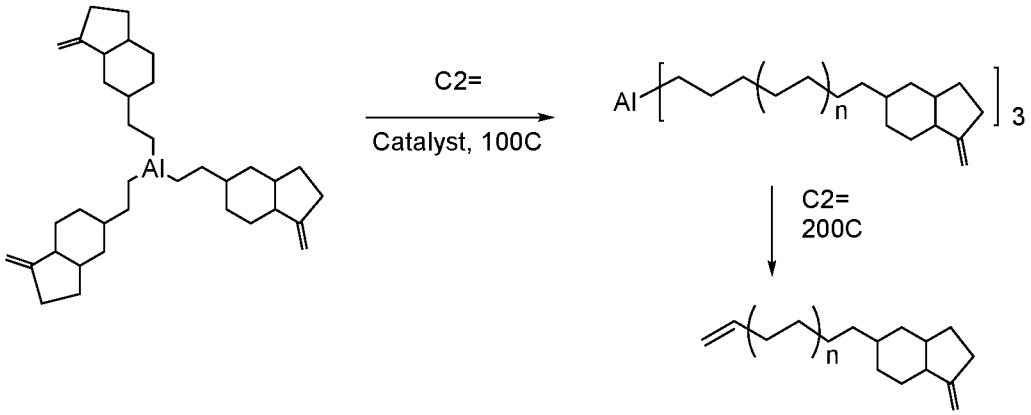
Run	Cat 1	CTA 5	Polymer (g)	Temp. (°C)	Mn, g/mol	Mw, g/mol	Mw/Mn
B1	4.5	-	43.0	120	72,542	739,532	10.2
B2	2.8	2	52.0	120	49,377	208,606	4.2
B3	1.5	2	37.6	120+200	37,531	169,615	4.5
B4	2.5	4	86.0	120	26,232	75,541	2.9
B5	1.5	4	76.0	120+200	22,630	78,956	3.5
B6	2.0	8	87.3	120	15,875	35,117	2.2
B7	1.0	8	119.0	120+200	12,239	31,477	2.6

Set 3

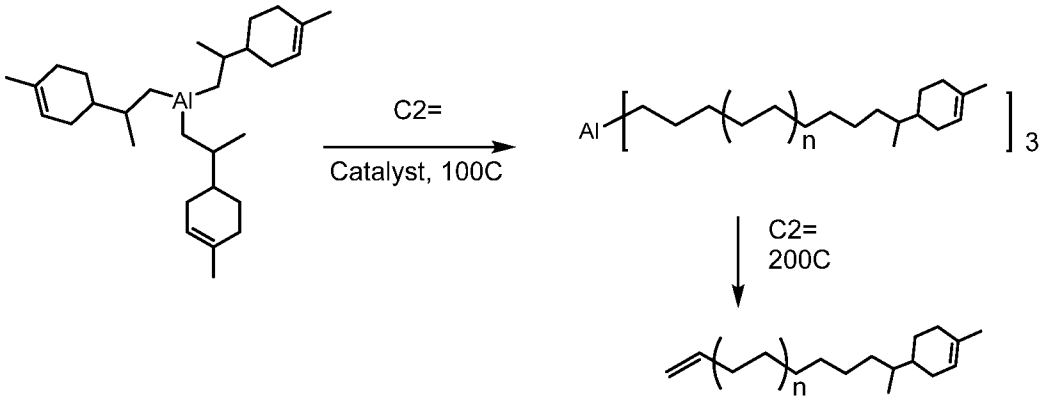
[0314] Set 3 includes the following examples to synthesize inventive telechelic polyethylene polymers.

[0315] In a nitrogen-filled drybox, a vial equipped with a stir-bar is charged with octene (10 mL), Cocat A (0.023 mL of 0.075 M solution, 0.0017 mmol,) and CTA 7 (0.402 mL of 0.5 M solution, 0.2 mmol). 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. Cat 13 (0.067 mL of 0.02 M solution, 0.0013 mmol) was injected, and the purge needle is removed to maintain a total pressure at 20 psig. The polymerization was maintained for 20 min, then the ethylene line was removed and the polymer solution was cooled down. This polymer solution was transferred to a 600 mL Parr reactor and sealed. The reactor was heated to 200 degree C under 200 psig of ethylene pressure for 30 min. Polymer was

quenched by large amount of methanol, filtrated and dried under vacuum overnight. 1H NMR (FIG. 3) confirmed the synthesis occurred via the non-limiting reaction scheme shown below.



[0316] In a nitrogen-filled drybox, a vial equipped with a stir-bar is charged with octene (10 mL), Cocat A (0.023 mL of 0.075 M solution, 0.0017 mmol,) and CTA 8 (0.088 g, 0.2 mmol). 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. Cat 13 (0.067 mL of 0.02 M solution, 0.0013 mmol) was injected, and the purge needle is removed to maintain a total pressure at 20 psig. The polymerization was maintained for 20 min, then the ethylene line was removed and the polymer solution was cooled down. This polymer solution was transferred to a 600 mL Parr reactor and sealed. The reactor was heated to 200 degree C under 200 psig of ethylene pressure for 30 min. Polymer was quenched by large amount of methanol, filtrated and dried under vacuum overnight. 1H NMR (FIG. 4) analysis confirmed the synthesis occurred via the non-limiting reaction scheme below.



Continuous Solution Polymerization

[0317] Non-limiting examples of the telechelic polyolefin of the formula $A^1L^1L^2A^2$ and the unsaturated polyolefin of the formula A^1L^1 were made via continuous solution polymerization as follows.

[0318] Continuous solution polymerizations are carried out in a computer controlled autoclave reactor equipped with an internal stirrer. Purified mixed alkanes solvent (Isopar™ E available from ExxonMobil), monomers, and molecular weight regulator (hydrogen or chain transfer agent) are supplied to a 3.8 L reactor equipped with a jacket for temperature control. The solvent feed to the reactor is measured by a mass-flow controller. A variable speed diaphragm pump controls the solvent flow rate and pressure to the reactor. At the discharge of the pump, a side stream is taken to provide flush flows for the procatalyst, activator, and chain transfer agent (catalyst component solutions) injection lines. These flows are measured by Micro-Motion mass flow meters and controlled by control valves. The remaining solvent is combined with monomers and hydrogen and fed to the reactor. The temperature of the solvent/monomer solution is controlled by use of a heat exchanger before entering the reactor. This stream enters the bottom of the reactor. The catalyst component solutions are metered using pumps and mass flow meters and are combined with the catalyst flush solvent and introduced into the bottom of the reactor. The reactor is liquid full at 500 psig with vigorous stirring. Polymer is removed through exit lines at the top of the reactor. All exit lines from the reactor are steam traced and insulated. The product stream is then heated at 230° C by passing through a post reactor heater (PRH) where beta-H elimination of polymeryl-Al takes place. A small amount of isopropyl alcohol is added along with any stabilizers or other additives either before the PRH (for the comparative examples) or after the PRH (for the inventive examples) before devolatilization. The polymer product is recovered by extrusion using a devolatilizing extruder.

[0319] The polymerization process conditions and results prior to post reactor heating (PRH) for the inventive and comparative examples are listed in Tables A1 to B2. Inventive unsaturated polyolefins of the formula $A^1L^1$are named as Inv. MP1 to MP4. Inventive telechelic polyolefins of the formula $A^1L^1L^2A^2$ are named as Inv. TP1 to TP10. Comparative polymers are named as Comp. A and B. Additional abbreviations in the tables are explained as follows: "Co." stands for comonomer; "sccm" stands for standard cm^3/min; "T" refers to temperature; "Cat" stands for Procatalyst; "Cat 1" stands for Procatalyst (Cat 1); "Cat 17" stands for Procatalyst (Cat 17), "Cocat" stands for Cocat A; "Al CTA" stands for aluminum chain transfer agent"; "TEA" stands

for triethylaluminum; "TOA" stands for trioctylaluminum, "Poly Rate" stands for polymer production rate; "Conv" stands for percent ethylene conversion in reactor; and "Eff." stands for efficiency, kg polymer/g catalyst metal.

[0320] In addition, [CTA]/[C_2H_4] refers to the molar ratio in reactor; Al/C_2 *1000 = (Al feed flow*Al concentration/1000000/Mw of Al)/(Total Ethylene feed flow*(1-fractional ethylene conversion rate)/Mw of Ethylene)*1000. "Al" in "Al/C_2*1000" refers to the amount of Al in the CTA used in the polymerization process, and "C2" refers to the amount of ethylene used in the polymerization process.

[0321] The properties of the inventive and comparative polymers following post reactor heating and recovery are provided in Tables C1-E2.

Table A1

	C2	Co. Type	Co.	Solv.	H_2	T	Cat. 1	Cat. 1 Flow
Ex.	lbs/hr		lbs/hr	lbs/hr	sccm	°C	ppm Hf	lbs/hr
Comp. A	1.375	Propylene	2.111	14.17	0	115	65.8	0.220
Inv. MP1	1.556	Propylene	1.641	13.93	0	115	65.8	0.225
Comp. B	1.520	Octene	1.362	14.98	352.7	115	65.8	0.286
Inv. MP2	1.521	Octene	1.520	15.01	0	115	65.8	0.170
Inv. MP3	3.33	Octene	3.60	29.26	0	115	125.5	0.212
Inv. MP4	2.78	Octene	2.41	30.44	0	115	63.2	0.385

Table A2

	CTA	CTA Conc.	CTA Flow	Cocat A	Cocat A Flow	$[C_2H_4]$/ [CTA]	Poly Rate	Conv	Solids	
Ex.		ppm Al	lbs/hr	ppm	lbs/hr		lbs/hr	%	%	Eff.
Comp. A	TEA	10000	0.928	922	0.126	51.1	2.2	86.3	14.3	0.154
Inv. MP1	TEA	10000	1.14	922	0.129	143.5	2.2	94.7	14.1	0.148
Comp. B	TEA	29.8	0.17	922	0.164	0.0	2.1	90.9	12.6	0.11
Inv. MP2	TEA	10000	0.43	922	0.098	17.3	1.82	83	13	0.194
Inv. MP3	TEA	9827	0.744	925	0.232	20.7	4.47	89.0	13.7	0.168
Inv. MP4	TEA	1920	0.723	894	0.219	21.6	3.72	97.6	8.4	0.114

Table B1

	C2	Co. Type	Co.	Solv.	H_2	T	Cat	Cat. Conc.	Cat. Flow
Ex.	Lbs/hr		lbs/hr	lbs/hr	sccm	°C		ppm Hf	lbs/hr
Comp. A	1.375	Propylene	2.111	14.17	0	115	Cat 1	65.8	0.22
Inv. TP1	1.555	Propylene	1.633	13.95	0	115	Cat 1	65.8	0.334
Inv. TP2	1.52	Propylene	1.768	14.1	0	115	Cat 1	65.8	0.326
Comp. B	1.52	Octene	1.362	14.98	352.7	115	Cat 1	65.8	0.286
Inv. TP3	1.519	Octene	1.415	14.93	0	115	Cat 1	65.8	0.204
Inv. TP4	1.506	Octene	1.657	19.44	0	115	Cat 1	65.8	0.18
Inv. TP5	2.78	Octene	2.62	25.5	0	115	Cat 1	63.2	0.475
Inv. TP6	4.76	Octene	5.46	41.78	0	118	Cat 1	125.5	0.328
Inv. TP7	2.56	Octene	3.39	17.40	0	115	Cat 1	125.5	0.199
Inv. TP8	3.84	Octene	1.07	42.19	0	125	Cat 14	54.2	0.149
Inv. TP9	2.78	Octene	2.67	29.52	0	115	Cat 1	63.2	0.372
Inv. TP10	5.55	Octene	4.45	59.08	0	119	Cat 1	63.2	1.002

Table B2

	CTA	CTA Conc.	CTA Flow	Cocat A	Cocat A Flow	$[C_2H_4]$/ [CTA]	Poly Rate	Conv	Solids	
Ex.		ppm Al	lbs/hr	ppm	lbs/hr		lbs/hr	%	%	Eff.
Comp. A	TEA	10000	0.928	922	0.126	51.1	2.2	86.3	14.3	0.154
Inv. TP1	CTA 1	69198	0.797	922	0.192	681.6	2.0	94.6	13	0.092
Inv. TP2	CTA 1	69198	0.78	922	0.187	594.4	2.7	93.8	17.1	0.125
Comp. B	TEA	29.8	0.17	922	0.164	0	2.1	90.9	12.6	0.11
Inv. TP3	CTA 1	69198	0.179	922	0.118	130.2	2.2	93.5	13.1	0.161
Inv. TP4	CTA 1	69198	0.077	922	0.103	33.1	2.0	88.9	9.7	0.174
Inv. TP5	CTA 2	2503	0.748	894	0.27	11.6	2.7	94.0	8.4	0.091
Inv. TP6	CTA 1	9432	0.420	925	0.359	7.8	6.4	88.9	13.8	0.157
Inv. TP7	CTA 1	18302	0.370	925	0.218	76.3	3.8	96.4	19.0	0.151
Inv. TP8	CTA 1	1478	0.210	495	0.131	0.8	3.5	89.8	7.5	0.431
Inv. TP9	CTA 1	3994	0.241	894	0.212	10.0	2.7	96.4	8.3	0.114
Inv. TP10	CTA 1	3994	0.467	894	0.570	11.6	5.5	97.0	8.6	0.087

Table C1

Method	Property	Units	Comp. A	Inv. MP1	Comp. B	Inv. MP2	Inv. MP3	Inv. MP4
13C NMR	%C2	mol%	70.1	76	89.4	88.7	89.1	88.3
13C NMR	%C3	mol%	29.9	24	--	--	--	--
13C NMR	%C8	mol%	--	--	10.6	11.3	10.9	11.7
1H NMR	Vinyls	#/1000000C	27	1076	14	441	295	291
1H NMR	Vinylidenes	#/1000000C	185	686	27	117	66	122
1H NMR	Vinylenes	#/1000000C	4	36	14	20	12	19
1H NMR	Cyclohexenes	#/1000000C	0	0	0	0	0	0
1H NMR	Trisubstituted alkenes	#/1000000C	4	31	7	15	6	10
13C NMR	Saturated CH3	#/1000000C	2050	1810	--	--	--	--
NMR	Unsaturations	#/1000C	0.22	1.8	0.06	0.58	0.379	0.442
Calculation	Unsats/chain	#/chain	0.17	1.06	0.11	1.30	0.68	1.39
Density		g/cc	--	--	0.873	0.872	0.873	0.8715
Melt Index	I2 at 190 °C	dg/min	--	--	18.3	17.6	30.8	5.1
Melt Index	I10/I2 at 190 °C		--	--	6.6	7.1	6.9	6.8
Brookfield	Viscosity @ 177 °C	cP	11,687	6,952	--	--	--	--

Table C2

Method	Property	Units	Comp. A	Inv. MP1	Comp. B	Inv. MP2	Inv. MP3	Inv. MP4
Conv. GPC	Mn	g/mol	9,244	7,239	19,618	22,862	18,823	32,689
Conv. GPC	Mw	g/mol	20,993	16,847	52,931	56,983	50,945	79,030
Conv. GPC	Mz	g/mol	44,770	34,657	92,282	122,456	129,351	157,436
Conv. GPC	Mw/Mn		2.27	2.33	2.7	2.49	2.71	2.42
DMS	Viscosity at 0.1 rad/s (190°C)	Pa-s	--	--	348	479	--	1513
DMS	Viscosity at 100 rad/s (190°C)	Pa-s	--	--	279	303	--	725
DMS	RR (V0.1/V100)		--	--	1.25	1.58	--	2.09
DMS	Tan Delta at 0.1 rad/s (190°C)		--	--	331	66.9	--	53.1
DMS	Tan Delta at 100 rad/s (190°C)		--	--	3.13	2.62	--	1.68
DSC	Tm	°C	-6.3	13.8	62.1	56.3	58.9	55.8
DSC	Tc	°C	-27.8	-3.5	48.6	61.2	68.3	61.7
DSC	Heat of Fusion	J/g	30.9	44.2	70.8	65	65.6	60.8
DSC	Wt% Crystallinity	%	10.6	15.1	24.3	22.3	22.5	20.8

Table D1

Polymer Properties								
Method	Property	Units	Comp. A	Inv. TP1	Inv. TP2	Comp. B	Inv. TP3	Inv. TP4
13C NMR	%C2	mol%	70.1	77.4	75.6	89.4	89	88.9
13C NMR	%C3	mol%	29.9	22.6	24.4	--	--	--
13C NMR	%C8	mol%	--	--	--	10.6	11	11.1
13C NMR	%ENB	Mol%	--	--	--	--	--	--
1H NMR	Vinyls	#/1000000C	27	1262	1222	14	444	207
1H NMR	Vinylidenes	#/1000000C	185	677	722	27	101	86
1H NMR	Vinylenes	#/1000000C	4	62	63	14	28	23
1H NMR	Cyclohexenes	#/1000000C	0	1720	1680	0	450	215
1H NMR	Trisubstituted alkenes	#/1000000C	4	37	34	7	8	7
13C NMR	Saturated CH3	#/1000000C	2050	640	440	--	--	--
NMR	Unsaturations	#/1000C	0.22	3.72	3.69	0.06	1.02	0.53
Calculation	Unsats/chain	#/chain	0.17	2.07	2.13	0.11	2.22	2.24
Density		g/cc	--	--	--	0.873	0.873	0.87
Melt Index	I2 at 190 °C	dg/min	--	--	--	18.3	16.8	0.9
Melt Index	I10/I2 at 190 °C		--	--	--	6.6	7	7.2
Brookfield	Viscosity @ 177 °C	cP	11,687	6,108	8,178	--	--	--

Table D2

Polymer Properties								
Method	Property	Units	Inv. TP5	Inv. TP6	Inv. TP7	Inv. TP8	Inv. TP9	Inv. TP10
13C NMR	%C2	mol%	87.9	88.9	87.9	98.2	88.6	88.6
13C NMR	%C3	mol%	--	--	--	--	--	--
13C NMR	%C8	mol%	12.1	11.2	12.1	1.8	11.4	11.5
13C NMR	%ENB	Mol%	--	--	--	--	--	--
1H NMR	Vinyls	#/1000000C	285	471	1239	283	307	288
1H NMR	Vinylidenes	#/1000000C	97	101	465	21	105	107
1H NMR	Vinylenes	#/1000000C	73	23	193	12	24	24
1H NMR	Cyclohexenes	#/1000000C		474	1473	278	302	318
1H NMR	Trisubstituted alkenes	#/1000000C	242	9	110	0	10	7
13C NMR	Saturated CH3	#/1000000C	--	--	--	--	--	--
NMR	Unsaturations	#/1000C	0.7	1.078	3.480	0.594	0.748	0.744
Calculation	Unsats/chain	#/chain	2.2	1.97	2.34	1.71	2.36	2.42
Density		g/cc	0.869	0.873	0.869	0.922	0.872	0.872
Melt Index	I2 at 190 °C	dg/min	5.4	27.3	--	1.9	4.7	5.3
Melt Index	I10/I2 at 190 °C		6.7	6.7	--	7.4	6.8	6.7
Brookfield	Viscosity @ 177 °C	cP	--	--	7906	--	--	--

Table E1

Polymer Properties								
Method	Property	Units	Comp. A	Inv. TP1	Inv. TP2	Comp. B	Inv. TP3	Inv. TP4
Conv. GPC	Mn	g/mol	9,244	6,925	7,149	19,618	22,713	43,792
Conv. GPC	Mw	g/mol	20,993	16,138	16,622	52,931	56,021	123,693
Conv. GPC	Mz	g/mol	44,770	39,246	47,921	92,282	129,181	283,832
Conv. GPC	Mw/Mn		2.27	2.33	2.33	2.7	2.47	2.83
DMS	Viscosity at 0.1 rad/s (190°C)	Pa-s	--	--	--	348	490	9,312
DMS	Viscosity at 100 rad/s (190°C)	Pa-s	--	--	--	279	302	1,903
DMS	RR (V0.1/V100)		--	--	--	1.25	1.63	4.89
DMS	Tan Delta at 0.1 rad/s (190°C)		--	--	--	331	52.9	10.1
DMS	Tan Delta at 100 rad/s (190°C)		--	--	--	3.13	2.65	0.934
DSC	Tm	°C	-6.3	17	10.1	62.1	58.4	53.3
DSC	Tc	°C	-27.8	-0.1	-7	48.6	64.4	58.9
DSC	Heat of Fusion	J/g	30.9	51.9	39.6	70.8	69.6	60.2
DSC	Wt% Crystallinity	%	10.6	17.8	13.6	24.3	23.8	20.6

Table E2

Method	Property	Units	Inv. TP5	Inv. TP6	Inv. TP7	Inv. TP8	Inv. TP9	Inv. TP10
Conv. GPC	Mn	g/mol	32,443	19,168	6,904	38,313	32,968	33,937
Conv. GPC	Mw	g/mol	79,907	49,328	15,631	99,196	82,260	78,203
Conv. GPC	Mz	g/mol	164,709	113,520	33,550	325,630	175,471	153,716
Conv. GPC	Mw/Mn		2.46	2.57	2.26	2.59	2.50	2.30
DMS	Viscosity at 0.1 rad/s (190°C)	Pa-s	1476	--	--	--	1735	--
DMS	Viscosity at 100 rad/s (190°C)	Pa-s	703	--	--	--	784	--
DMS	RR (V0.1/V100)		2.1	--	--	--	2.21	--
DMS	Tan Delta at 0.1 rad/s (190°C)		54.3	--	--	--	42.8	--
DMS	Tan Delta at 100 rad/s (190°C)		1.66	--	--	--	1.61	--
DSC	Tm	°C	50	56.5	51.8	114.5	54.6	55.5
DSC	Tc	°C	54.2	67.3	34.9	103.7	58.7	54.1
DSC	Heat of Fusion	J/g	55.2	69.3	55.7	130.4	58.6	59.1
DSC	Wt% Crystallinity	%	18.9	23.7	19.1	44.7	20.1	20.2

[0322] As seen in the above tables, ^{1}H NMR and ^{13}C NMR analyses confirm the synthesis of new telechelic polyolefins TP1 to TP10 via the inventive process of the present disclosure. Specifically, as one of ordinary skill in the art would understand, ^{1}H NMR and ^{13}C NMR analyses confirm formation of new telechelic polyolefins for TP1 to TP10, where such polyolefins have unsaturations at both ends. Specifically, such polyolefins have A^1 groups (vinyls, vinylenes, vinylidenes) on one end with A^2 groups having hindered double bonds (cyclohexenes or trisubstituted alkenes) on the other end. In contrast, comparative polymers A and B, which were not prepared according to the inventive process of the present disclosure, are polymers with low unsaturation as seen via ^{1}H NMR and ^{13}C NMR analyses.

[0323] In Inv. TP5, the hindered double bond of the A2 group is a trisubstituted unsaturation, resulting in a high number of trisubstituted unsaturations/1000000C as reported in the above tables. The number of trisubstituted unsaturations in TP5 is higher than for Comparative B that was produced with the same catalyst under similar reactor conditions, but with hydrogen to control molecular weight. A small number of trisubstituted unsaturations can be formed via beta-hydride elimination and subsequent rearrangement of the unsaturation in an ethylene/alpha-olefin. The number of trisubstituted unsaturations formed by this thermal termination mechanism is dependent on the catalyst and process conditions used. A small number of trisubstituted unsaturations from this thermal termination mechanism is present in all of the comparative and inventive examples, but at a lower level than the vinyls and vinylidenes, with the exception of TP5 where the majority of the trisubstituted unsaturations are from the A2 group.

[0324] As described above, the novel telechelic polyolefins of the present disclosure contain unsaturations at the termini of the chains rather than randomly distributed along the polymer backbone. Such telechelic polyolefins may be suitable for curable formulations and may improve crosslinking. By controlling the location of the unsaturations to the polymer chain ends, a more controlled network structure is formed (uniform Mw between crosslinks) and more efficient use is made of the unsaturations on the polymer chain. This should provide better thermal and UV aging stability as less unsaturations are needed to form a cross-linked network with good mechanical properties for a given molecular weight. A low viscosity of a low Mw telechelic polyolefin of the present disclosure would provide excellent processability and flow prior to crosslinking, unlike high Mw EPDM.

[0325] In addition, the telechelic polyolefins of the present disclosure are produced in a low cost solution polymerization from ethylene and alpha-olefins that is unique from telechelic polyolefins that have been produced in the literature via much more expensive and complicated synthetic routes. Further, the telechelic polyolefins also enable the opportunity for controlled chain extension to a higher molecular weight thermoplastic unlike random copolymers with unsaturations. Because the unsaturations are located at the chain ends, the telechelic polyolefins can be chain extended to form a high molecular weight thermoplastic resin. Suitable crosslinking and chain extension chemistry includes, but is not limited to peroxide, thiolene, sulfur cure, phenolic cure, etc.

Curable Compositions for Crosslinked Foams

[0326] The following non-limiting examples demonstrate the inventive curable compositions for crosslinked foams of the present disclosure, where the inventive curable compositions include the inventive polyolefins TP1 and TP7.

[0327] The following materials were also used in the following examples:

[0328] AFFINITY™ GA 1900: an ethylene/1-octene copolymer having a density of 0.870 g/cm^3 (ASTM D792) and a Brookfield viscosity of 8200 cP (ASTM D3236, 177 °C) available from The Dow Chemical Company.

[0329] INFUSE™ 9100: an olefin block copolymer having a density of 0.877 g/cm^3 (ASTM D792) and a melt index of 1.0 g/10 min (ASTM D1238, 190°C/2.16 kg) available from The Dow Chemical Company.

[0330] Perkadox® 14 SFL: α,α'-Bis(tert-butylperoxy) diisopropylbenzene (BIPB) with active peroxide content around 99 wt% available from HM Royal.

[0331] AC9000: Azodicabonamide type blowing agent from Kumyang

[0332] TiO_2: Ti-Pure® R-103 from Chemours

[0333] Zinc Oxide and Zinc Stearate.

Compound Preparation

[0334] Polymer pellets were added to the 350ml Brabender mixer. Then, ZnO, ZnSt and TiO_2 were added after the polymer had melted (around 5 minutes). The blowing agent and peroxide were added last after the fillers were uniformly dispersed and mixed for another 3 to 5 minutes for a total mix time of 15 minutes. The batch temperature was checked by using an immersion thermo probe detector right after the compounds were discharged. The compounds' actual

temperature is generally 10 to 15 °C higher than the displayed temperature on the equipment. Hence, during the compounding process, it is better to control the displayed equipment temperature lower to ensure the compound temperature does not exceed the curing agent and blowing agent decomposition temperature. The batch is then quickly transferred to a two-roll mill that is heated to 90 – 105 °C as passed through the roll mill three to four times, folding mill sheet over on itself between each pass, to obtain a roll milled blanket.

Bun Foam Preparation

[0335] Roll milled blankets were cut into squares and placed inside a pre-heated bun foam mold. The surface of the chase was sprayed with mold releasing agent to avoid sticking of the foam to the chase during de-molding. Two compression molding processes were involved: preheating first to eliminate air pockets inside the sample and between the stacked layers prior to curing, and then curing/foaming. The preheating was conducted for 8 minutes at 120 °C and pressed at 10 tons for 4 minutes to form a solid mass in the mold before foaming. The preheated mass was transferred to the foaming press and held for 8 minutes at 100 kg/cm^2 and 180 °C. Once the pressure was released, the bun foam was removed quickly from the tray and placed in a vent hood on several non-stick sheets and the top side length is measured as soon as possible. The foam surfaces were insulated from the bench top using cardboard boxes. Insulating the surfaces of the newly made bun foam prevented uneven cooling on the top and bottom surface. The foams cooled in the hood for 40 minutes then were transferred to a storage container and allowed to cool for 24 hours. The length was then measured again and the foam expansion ratio can be calculated (length of the cool foam/length of the mold).

Foam Cutting and Slicing

[0336] The foam slabs were first cut into 6"x6" plaques using a vertical band saw. Hardness and Rebound of the foam plaques (with skin) were measured. Thin slices (thickness around 3 mm) including the skin layers and foam layers were then cut from the plaques by using a lab scale horizontal band saw. The slices would be further used to measure the tear properties.

Curable Compositions for PV Encapsulant Films

[0337] The following non-limiting examples demonstrate the inventive curable compositions of the present disclosure, where the inventive curable compositions include the inventive polyolefins TP1, TP3, TP6, TP7, MP1, MP2, or MP3.

[0338] The following materials were also used in the following examples:

[0339] XUS 38661.00 Polyolefin Elastomer (XUS 38661): an ethylene/1-octene copolymer having a density of 0.880 g/cm^3 (ASTM D792) and a melt index of 18.0 g/10 min (ASTM D1238, 190°C/2.16 kg) available from The Dow Chemical Company.

[0340] ENGAGE™ 8407: an ethylene/1-octene copolymer having a density of 0.870 g/cm^3 (ASTM D792) and a melt index of 30.0 g/10 min (ASTM D1238, 190°C/2.16 kg) available from The Dow Chemical Company.

[0341] AFFINITY™ GA 1900: an ethylene/1-octene copolymer having a density of 0.870 g/cm^3 (ASTM D792) and a Brookfield viscosity of 8200 cP (ASTM D3236, 177 °C) available from The Dow Chemical Company.

[0342] "TBEC": Tert-Butylperoxy 2-ethylhexyl carbonate, peroxide available from J&K Scientific Ltd.

[0343] "TAIC": Triallyl isocyanurate, coagent available from Fangruida Chemicals Co., Ltd.

[0344] "VMMS": 3-(trimethoxysilyl)propylmethacrylate, silane coupling agent available as VMMS from Dow Corning.

[0345] T770: Ultraviolet (UV) absorber, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, available from Alfa Aesar.

Sample Preparation

[0346] Compounding: For samples with multiple polymer resin components, the polymer resins were compounded on a twin screw extruder. The polymer pellets were dry blended and then fed into a 20 mm Brabender twin screw extruder and compounded at 100 rpm and 110 °C. The extruded polymer blend strands were passed through a water bath to cool and pelletized.

[0347] Soaking: The liquid additives, including peroxides, silanes and coagents were weighed and mixed in a sealable plastic bottle. About 50 g of polymer pellets were weighed and placed in a 250 mL fluorinated high density polyethylene bottle containing the liquid additives. To ensure a homogenous distribution and complete soaking of the additives into the pellets, the bottle was placed on a running roller (Model No. 88881004, Thermo Scientific) for at least one hour in an oven at 40 °C. The sample was then kept in oven at 40 °C for 5 - 20 hours with periodic shaking until no liquid residues were visually seen adhering to the bottle before using the samples for MDR analysis.

[0348] Film Lamination: The pellets after soaking were fed into a Brabender single screw mixer at 110 °C with a rotor speed of 40 rpm. Stripes with a thickness of around 0.5 mm were prepared and kept in an aluminum foil bag for subsequent lamination for gel tests. The lamination is conducted with a laminator (SHUNHONG SH-X-1000 laminator). A piece 0.5 mm thick film of the curable composition is placed on a polytetrafluoroethylene (PTFE) film (0.15 mm thick) on a glass substrate (3 mm thick). Another PTFE film (0.15 mm thick) is placed on top of the sample. Samples were laminated at 150 °C using a two step method: 1) 4 min of preheating under vacuum without pressure; and 2) curing for 6 to 12 min with 1 bar pressure. Thus total lamination times were 10 (4+6) min, 12 (4+8) min, and 16 (4+12) min. The laminated samples were used for gel test.

Performance and Properties

[0349] Tables HF1-HF3 shown below report the curing levels of the exemplary curable compositions and the mechanical properties of the resulting crosslinked foams. IE indicates inventive curable compositions and crosslinked foams according to the present disclosure. CE indicates comparative examples that represent the state of the art with respect to curable compositions and crosslinked foams.

Table HF1.

Example	CE-4	CE-6	IE-15	IE-16	IE-17	IE-18	CE-7
INFUSE™ 9100 wt%	94.69	85.10	85.27	85.22	89.48	85.27	75.82
TP1 wt%			9.47				
TP7 wt%				9.47	4.97	9.47	18.96
AFFINITY GA 1900 wt%		9.46					

BIPB wt%	0.57	0.71	0.52	0.57	0.57	0.52	0.47
AC9000 wt%	2.37	2.36	2.37	2.37	2.49	2.37	2.37
ZnO wt%	0.24	0.24	0.24	0.24	0.25	0.24	0.24
ZnSt wt%	0.24	0.24	0.24	0.24	0.25	0.24	0.24
TiO2 wt%	1.89	1.89	1.89	1.89	1.99	1.89	1.90
Properties							
MH-ML, dN.m	2.9	2.7	3.0	3.2	3.1	3.0	2.4
Viscosity at 130 °C and 100 rad/s, Pa-s	2806	2219	2264	2454	2729	2463	1931
Expansion ratio	151%	149%	147%	149%	152%	153%	165%
Hardness, Asker C	57	54	55	58	55	54	43
Rebound, %	65	66	68	68	68	68	68
Type C tear, N/mm	11.5	9.9	11.1	12.1	10.9	10.7	8.8
Shrinkage	1.2%	1.7%	1.3%	1.4%	1.4%	1.1%	1.1%

Table HF2

Example	CE-2A	CE-4	IE-15	IE-16	IE-18	IE-19	IE-21	IE-22
Formulation, wt%								
XUS 38661.00	98.18	88.36	88.36	88.36				
TP3					88.36	88.36		
MP2							88.36	88.36
AFFINITY GA 1900		9.82						
TP1			9.82		9.82		9.82	
MP1				9.82		9.82		9.82
TBEC	1	1	1	1	1	1	1	1
TAIC	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
VMMS	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
T770	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Properties								
MH-ML, dNm	3.4	2.7	3.0	3.2	4.7	4.8	5.2	5.1
Viscosity at 110 °C and 100 rad/s, Pa-s	1177	1131	972	980	1046	1057	1051	1041

Table HF3

Example	CE-3B	CE-5	CE-6	IE-23	IE-24	IE-25	IE-27
Formulation, wt%							
ENGAGE 8407	98.18	93.27	88.36	93.27	88.36		
MP3						88.36	
TP6							88.36
TP7				4.91	9.82	9.82	9.82

AFFINITY GA 1900		4.91	9.82				
TBEC	1	1	1	1	1	1	1
TAIC	0.5	0.5	0.5	0.5	0.5	0.5	0.5
VMMS	0.25	0.25	0.25	0.25	0.25	0.25	0.25
T770	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Properties							
MH-ML, dNm	2.9	2.6	2.3	2.8	2.6	5.3	4.2
Viscosity at 110 °C and 100 1/s, Pa-s	981	884	771	846	768	751	657

[0350] As seen in Tables HF1-HF3, the inventive curable compositions comprising the high flow telechelic polyolefin and/or the unsaturated polyolefin of the present disclosure surprisingly and unexpectedly demonstrate low viscosity, while maintaining or improving the curing level obtained with comparable or even less crosslinking agent compared to the comparative exmaples representing the state of the art for crosslinked foams (Table HF1) or for PV encapsulants (Tables HF2-HF3). Crosslinked foams prepared from the inventive curable compositions surprisingly demonstrate improved or similar mechanical performance at the same expansion ratio range compared to the comparative examples representing the state of the art. Accordingly, it is clear from these unexpected results that inventive curable compositions of the present disclosure address the need for lower viscosity, while maintain cure level and mechanical properties, which can lead to faster processing (such as extrusion) and shorter cycle times for preparing curable formulations for applications including footwear foams and PV encapsulants, while retaining the advantages of polyolefins in mechanical performance.

What is claimed is:

1. A crosslinked foam article made from a curable composition comprising (A) a polyolefin component comprising a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP; wherein the viscosity is a Brookfield viscosity (as measured at 177 °C) in accordance with ASTM-D3236 and (B) a curing component comprising a cross-linking agent, wherein:

L^1 is a polyolefin;

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

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

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

A^2 is a hydrocarbyl group comprising a hindered double bond; and wherein the (A) polyolefin component is present in an amount of from 4 wt% to 15 wt%, based on the total weight of the curable composition.

2. A crosslinked foam article made from a curable composition comprising (A) a polyolefin component comprising an unsaturated polyolefin of the formula A^1L^1 that has a viscosity less than 100,000 cP and a telechelic polyolefin of the formula $A^1L^1L^2A^2$ that has a viscosity less than 100,000 cP; wherein the viscosity is a Brookfield viscosity (as measured at 177 °C) in accordance with ASTM-D3236 and (B) a curing component comprising a cross-linking agent, wherein:

L^1 at each occurrence independently is a polyolefin;

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

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

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

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

A^2 is a hydrocarbyl group comprising a hindered double bond; and wherein the (A) polyolefin component is present in an amount of from 4 wt% to 15 wt%, based on the total weight of the curable composition.

3. The curable composition of claim 1 or 2, wherein the telechelic polyolefin has a weight average molecular weight from 1,000 to 40,000 g/mol.

4. The curable composition of claim 2, wherein the unsaturated polyolefin has a weight average molecular weight from 1,000 to 40,000 g/mol.

5. The curable composition of any of the previous claims, wherein the curable composition further comprises (C) an additive component and (D) an ethylene-based polymer.

6. The curable composition of claim 5, wherein the ethylene-based polymer is an ethylene/alpha-olefin copolymer or an olefin block copolymer.

7. The curable composition of claim 5 or 6, wherein the (C) additive component comprises a blowing agent.

8. The curable composition of any of the previous claims, wherein the curable composition has a viscosity (at 100 rad/s and 130 °C) from less than or equal to 2800 Pa-s before curing and an MH-ML of greater than or equal to 3.0 dNm after curing at 180°C for 15 minutes.

9. The curable composition of any of claims 2-8, wherein L^1 of the unsaturated polyolefin of the formula A^1L^1 is covalently bonded to A^1 through a carbon-carbon single bond.

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