Although these CSAs can be considered to contain multiple sites, for example diethyl zinc contains two zinc-ethyl moieties from which a polymer can be attached, chain shuttling between the CSA and catalyst occurs in one direction on each polymer chain. The use of dual-headed CSAs containing an equal number of zinc-alkyl and zinc-alkdiyl groups can potentially lead to reduced homogeneity in the polymer architecture. Such materials can also lead to a broadening of product molecular weight distribution.

[0005] Even with the advent of CSA-dual catalyst combinations in block-copolymer preparation, there remain challenges in tailoring the specific copolymer properties that one desires using this approach. Therefore, it is desirable to develop new chain shuttling agents, methods of making the chain shuttling agents, as well as new CSA-catalyst combinations, that can provide new methods to prepare block-copolymers and copolymers with improved properties.

SUMMARY ~~OF THE INVENTION~~

[0006] In one aspect~~some embodiments~~, there is~~the present disclosure~~ provide~~s for~~ a chain shuttling agent having the formula:

$$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1,$$

$$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2,$$

$$M^C[R^2]_2M^C, \text{ or}$$

$$M^B[R^2]_3M^B;$$

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, ~~Al,~~ or Ga;

M^C is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$;

wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and N, on average, in each occurrence is a number from 2 to 150, inclusive.

[0007] In practice, N is the average that describes a sample of molecules and will not necessarily be an integer. For example, N on average can be a number from 5 to 140, from 10 to 125, from 15 to 110, or from 20 to 100, inclusive. The N value of a sample can be determined by NMR spectroscopy or comparable methods.

[0008] In these shuttling agent formulas, R^1 generally can be selected from any monovalent moiety that does not prevent chain shuttling from occurring. By way of example, R^1 is typically selected from a hydrocarbyl such as an alkyl having from 1 to 20 carbon atoms. Also by way of example, R^2 can be selected independently from ethandiyl, 1,3-propandiyl, 1,4-butandiyl, 1,5-pentandiyl, 1,6-hexandiyl, 2,5-hexandiyl, 1,7-heptandiyl, 1,8-octandiyl, 1,9-nonandiyl, 1,10-decandiyl, and the like.

[0008a] In another aspect, there is provided a multiblock copolymer obtained by a process comprising: contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions; wherein the catalyst composition comprises the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and a chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$,

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$,

$M^C[R^2]_2M^C$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, Al, or Ga;

M^c is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

[0009] In some embodiments, the present disclosure provides for a process for making the chain shuttling agents having the formula $R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$, $R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, $M^C[R^2]_2M^C$, or $M^B[R^2]_3M^B$, as described above.

[0009a] In another aspect, there is provided a catalyst composition comprising the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and a shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$,

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$,

$M^C[R^2]_2M^C$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, Al, or Ga;

M^c is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

[00010] In some embodiments, the present disclosure provides for a catalyst composition comprising the contact product at least one polymerization catalyst precursor, at least one cocatalyst, and at least one shuttling agent as described above. In other embodiments, the present disclosure provides for a process for preparing a catalyst component, the process comprising contacting at least one polymerization catalyst precursor, at least one cocatalyst, and at least one shuttling agent having the formula $R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$, $R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, $M^C[R^2]_2M^C$, or $M^B[R^2]_3M^B$, as described above.

[00011] In another aspect~~some embodiments~~, there is~~the present disclosure~~ provided~~s for~~ a process for the polymerization of at least one addition polymerizable monomer to form a polymer composition, the process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions;

wherein the catalyst composition comprise~~sing~~ the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and the~~at least one~~ shuttling agent~~ having the formula $R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$, $R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, $M^C[R^2]_2M^C$, or~~

~~$M^B[R^2]_2M^B$,~~ as described above.

[00012] In another~~one~~ aspect, there is~~this disclosure~~ provide~~d~~s a chain shuttling agent represented by the following Newkome dendrimer nomenclature:

$$[C][(R)^G_{N_b}(Z)]_{N_c},$$

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein:

C is a core selected from a metal, alkdiyl di(metal), alktriyl tri(metal), or alktetrayl tetra(metal), wherein the metal is Zn, Mg, B, Al, or Ga, and any carbon-containing core having from 2 to 50 carbon atoms;

R in each occurrence is a repeat unit selected from an alkdiyl metal, alktriyl di(metal), or alktetrayl tri(metal) having from 2 to 20 carbon atoms and an average branch multiplicity of N_b;

G is the generation of the dendrimer cascade;

Z is a terminal monovalent group having up to 20 carbon atoms;

N_C is the branch multiplicity of the core; and

the shuttling agent comprises at least one generation of repeat unit R, such that G, on average, is an number from 2 to 150, inclusive.

[00013] In practice, G is the average generational description of a sample of molecules and will not necessarily be an integer. The G and N of a sample can be determined by NMR spectroscopy or comparable methods.

[00013a] In another aspect, there is provided a multiblock copolymer obtained by the process as defined above.

[00014] This disclosure also provides a process for the polymerization of at least one addition polymerizable monomer to form a polymer composition, the process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions;

the catalyst composition comprising the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and at least one chain shuttling agent as described above.

[00015] In another aspect, there is~~This disclosure also~~ provide~~d~~s ~~for~~ a catalyst composition comprising the contact product ~~of~~ least one polymerization catalyst precursor, at least one cocatalyst, and the~~at least one~~ shuttling agent as defined~~represented by the Newkome dendrimer nomenclature~~ above. This disclosure also provides for a process for preparing such a catalyst component, the process comprising contacting at least one polymerization catalyst precursor, at least one

cocatalyst, and at least one shuttling agent of this Newkome dendrimer nomenclature.

[00015a] In another aspect, there is provided a process for preparing the chain shuttling agent as defined above comprising:

a) providing a polyene having the formula $R^AC[(CH_2)_nCH=CH_2]_3$ or $C[(CH_2)_nCH=CH_2]_4$, wherein n in each occurrence is independently an integer from 0 to 20 and R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

b) contacting the polyene with a borohydride having the formula $(R^C)_2BH$, wherein R^c is a hydrocarbyl having from 1 to 20 carbon atoms, to form a first composition comprising a partially hydroborated polyene;

c) contacting the first composition with $M^A(R^{1A})_2$ or $M^B(R^{1A})_3$ to form a second composition, comprising $M^A\{CH_2CH_2(CH_2)_nE[(CH_2)_nCH=CH_2]_{m-1}\}_2$ or $M^B\{CH_2CH_2(CH_2)_nE[(CH_2)_nCH=CH_2]_{m-1}\}_3$, wherein R^{1A} in each occurrence is independently a hydrocarbyl having from 1 to 20 carbon atoms, inclusive, optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide;

d) contacting the second composition with $(R^C)_2BH$, followed by contacting the resulting composition with $M^A(R^{1A})_2$ or $M^B(R^{1A})_3$ to form a third composition;

e) contacting the third composition with a partially hydroborated polyene prepared according to step b); and

f) repeating steps d) and e) any number of times to form a dendrimeric chain shuttling agent.

[00016] In some embodiments, the present disclosure provides for a process for making the chain shuttling agents having the formulas $[C][(R)^G_{N_b}(Z)]_{N_c}$, as described above.

[00017] While the Newkome nomenclature is not a molecular formula in the traditional sense, it does constitute a shorthand by which one of ordinary skill in the art can understand the traditional molecular formula. According to the Newkome nomenclature parameters, because G is an number from 2 to 150, there is at least one repeat unit in the dendritic chain shuttling agent of this disclosure.

[00017a] In another aspect, there is provided a process for preparing a chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$, wherien M^A is Zn or Mg, or

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, wherein M^B is B, Al, or Ga;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; the process comprising:

a) providing an α,ω-diene having the formula $CH_2{=}CH(CH_2)_nCH{=}CH_2$, $O[(CH_2)_nCH{=}CH_2]_2$, $S[(CH_2)_nCH{=}CH_2]_2$, $R^AN[(CH_2)_nCH{=}CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH{=}CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH{=}CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH{=}CH_2]_2O$; wherein n in each occurrence is independently an integer from 0 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive;

b) contacting the α,ω-diene with a borohydride compound having the formula $(R^C)_2BH$, wherein R^c is a hydrocarbyl having from 1 to 20 carbon atoms, to form a first composition; and

c) contacting the first composition with $M^A(R^{1A})(R^1)$ or $M^B(R^{1A})(R^1)_2$ to form a second composition comprising the chain shuttling agent;

wherein

R^{1A} in each occurrence is independently selected from hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, inclusive, optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

[00017b] In another aspect, there is provided a chain shuttling agent having the formula:

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^B is Al;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 3 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

[00018] As understood by one of ordinary skill, the branch multiplicity of the core (N_c) is two for zinc and for an alkdiyl di(metal), three for an alktriyl tri(metal), and four for an alktetrayl tetra(metal). However, the branch multiplicity N_b of the repeat unit R is one for an alkandiyl metal, two for an alkantriyl di(metal), and three for an alkantetrayl tri(metal).

[00019] Another embodiment~~aspect~~ of this disclosure is that the chain shuttling agents such as $R^1[M^A\text{-}R^2\text{-}]_N\text{-}M^AR^1$ and $R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$ disclosed herein constitute CSAs that typically can be described by the Newkome dendrimer nomenclature $[C][(R)^G_{N_b}(Z)]_{N_c}$.

[00020] A further embodiment~~aspect~~ of this disclosure relates to the preparation and utility of catalyst compositions having new structural entities containing repeating units of main group metals and alkandiyl groups, such as -alkandiyl-zinc-alkandiyl-zinc-alkandiyl-, and so forth. Such structures can function as dual headed CSAs and can be used in block-type polymerization reactions. For example, when the monomer feed or concentration is altered during a copolymerization process, symmetric gradient triblock copolymers can be formed. The process can be extended to form a symmetric multiblock copolymer with an odd number of blocks, with those blocks having either a gradual or a sharp gradient in composition or crystallinity. In a further embodiment~~aspect~~, this disclosure provides for compositions comprising or selected from the polymeric and heteroatom substituted CSAs disclosed herein, and processes for making and using them, and compositions of the product polymers.

[00021] Accordingly, one embodiment~~aspect~~ of the present disclosure provides an olefin polymer composition characterized by a narrow molecular weight distribution and a process for preparing the olefin polymer composition. The polymer compsition is

prepared in situ by the polymerization of one or more addition polymerizable monomers, generally of two or more addition polymerizable monomers, particularly ethylene and at least one copolymerizable comonomer, propylene and at least one copolymerizable comonomer having 4 or more carbons, or 4-methyl-1-pentene and at least one different copolymerizable comonomer having 4 or more carbons, optionally comprising multiple blocks or segments of differentiated polymer composition or properties, especially blocks or segments comprising differing comonomer incorporation levels. In this embodiment~~aspect~~, the present process includes contacting an addition polymerizable monomer or mixture of monomers under addition polymerization conditions with a composition comprising at least one addition polymerization catalyst, a cocatalyst and a dual-headed or multi-headed chain shuttling agent as provided herein.

[00022] Further, this disclosure provides a process for forming an n-block copolymer where n is an odd number greater than or equal to 3, the process comprising contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions; the catalyst composition comprising at least one polymerization catalyst precursor, at least one cocatalyst, and at least one shuttling agent as disclosed herein; wherein the process comprises (n+1)/2 combination chain transfer and growth steps.

DETAILED DESCRIPTION OF THE INVENTION

[00023] The term "shuttling agent" or "chain shuttling agent" refers to a compound or mixture of compounds that is capable of causing polymeryl transfer between various active catalyst sites under conditions of polymerization. That is, transfer of a polymer fragment occurs both to and from an active catalyst site in a facile and reversible manner. In contrast to a shuttling agent, an agent that acts merely as a chain transfer agent such as some main-group alkyl compounds, may exchange, for example, an alkyl group on the chain transfer agent with the growing polymer chain on the catalyst, which generally results in termination of the polymer chain growth. In this event, the main-group center may act as a repository for a dead polymer chain, rather than engaging in reversible transfer with a catalyst site in the manner in which the chain shuttling agent does. Desirably, the intermediate formed between the chain shuttling agent and the polymeryl chain is not sufficiently stable relative to exchange between this intermediate and any other growing polymeryl chain, such that chain termination is relatively rare.

[00024] The multi- or dual-headed shuttling agents include species with metal-

CLAIMS

We Claim:

1. A chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$,

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$,

$M^C[R^2]_2M^C$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, Al, or Ga;

M^C is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

2. A process for the polymerization of at least one addition polymerizable monomer to form a polymer composition, the process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions; wherein

the catalyst composition comprises the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and the chain shuttling agent of Claim 1.

3. A multiblock copolymer obtained by the process of Claim 2.

4. A catalyst composition comprising the contact product at least one polymerization catalyst precursor, at least one cocatalyst, and the shuttling agent of Claim 1.

5. A chain shuttling agent represented by the following Newkome dendrimer nomenclature:

$$[C][(R)^{G}N_b(Z)]N_c,$$

an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein:

C is a core selected from a metal, alkadiyl di(metal), alkatriyl tri(metal), or alkatetrayl tetra(metal), wherein the metal is Zn, Mg, B, Al, or Ga, and any carbon-containing core has from 2 to 20 carbon atoms;

R in each occurrence is a repeat unit selected from an alkadiyl metal, alkatriyl di(metal), or alkatetrayl tri(metal) having from 2 to 20 carbon atoms and a branch multiplicity of N_b;

G is the generation of the dendrimer cascade;

Z is a terminal monovalent having up to 20 carbon atoms;

N_c is the branch multiplicity of the core; and

the shuttling agent comprises at least one generation of repeat unit R, such that G on average is a number from 2 to 150, inclusive.

6. A process for the polymerization of at least one addition polymerizable monomer to form a polymer composition, the process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions;

wherein the catalyst composition comprises the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and the shuttling agent of Claim 5.

7. A multiblock copolymer obtained by the process of Claim 6.

8. A catalyst composition comprising the contact product at least one polymerization catalyst precursor, at least one cocatalyst, and the shuttling agent of Claim 5.

9. A process for preparing the chain shuttling agent of Claim 5 comprising:

a) providing a polyene having the formula $R^{A}C[(CH_2)_nCH=CH_2]_3$ or

$C[(CH_2)_nCH=CH_2]_4$, wherein n in each occurrence is independently an integer from 0 to 20 and R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

b) contacting the polyene with a borohydride having the formula $(R^C)_2BH$, wherein R^C is a hydrocarbyl having from 1 to 20 carbon atoms, to form a first composition comprising a partially hydroborated polyene;

c) contacting the first composition with $M^A(R^{1A})_2$ or $M^B(R^{1A})_3$ to form a second composition, comprising $M^A\{CH_2CH_2(CH_2)_nE[(CH_2)_nCH=CH_2]_{m-1}\}_2$ or $M^B\{CH_2CH_2(CH_2)_nE[(CH_2)_nCH=CH_2]_{m-1}\}_3$, wherein R^{1A} in each occurrence is independently a hydrocarbyl having from 1 to 20 carbon atoms, inclusive, optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide;

d) contacting the second composition with $(R^C)_2BH$, followed by contacting the resulting composition with $M^A(R^{1A})_2$ or $M^B(R^{1A})_3$ to form a third composition;

e) contacting the third composition with a partially hydroborated polyene prepared according to step b); and

f) repeating steps d) and e) any number of times to form a dendrimeric chain shuttling agent.

10. A process for preparing a chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$, wherien M^A is Zn or Mg, or

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, wherein M^B is B, Al, or Ga;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; the process comprising:

a) providing an α,ω-diene having the formula $CH_2=CH(CH_2)_nCH=CH_2$, $O[(CH_2)_nCH=CH_2]_2$, $S[(CH_2)_nCH=CH_2]_2$, $R^AN[(CH_2)_nCH=CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH=CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH=CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH=CH_2]_2O$; wherein n in each occurrence is independently an integer from 0 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive;

b) contacting the α,ω-diene with a borohydride compound having the formula $(R^C)_2BH$, wherein R^C is a hydrocarbyl having from 1 to 20 carbon atoms, to form a first composition; and

c) contacting the first composition with $M^A(R^{1A})(R^1)$ or $M^B(R^{1A})(R^1)_2$ to

form a second composition comprising the chain shuttling agent;

wherein

R^{1A} in each occurrence is independently selected from hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, inclusive, optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

CLAIMS

1. A chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$,

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$,

$M^C[R^2]_2M^C$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, or Ga;

M^c is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

2. A process for the polymerization of at least one addition polymerizable monomer to form a polymer composition, the process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions; wherein

the catalyst composition comprises the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and the chain shuttling agent of claim 1.

3. A multiblock copolymer obtained by a process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions; wherein

the catalyst composition comprises the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and a chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$,

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$,

$M^C[R^2]_2M^C$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, Al, or Ga;

M^c is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

4. A catalyst composition comprising the contact product at least one polymerization catalyst precursor, at least one cocatalyst, and a shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$,

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$,

$M^C[R^2]_2M^C$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^A is Zn or Mg;

M^B is B, Al, or Ga;

M^c is Mg;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

5. A chain shuttling agent represented by the following Newkome dendrimer nomenclature:

$[C][(R)^G_{N_b}(Z)]N_c$,

an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein:

C is a core selected from a metal, alkadiyl di(metal), alkatriyl tri(metal), or alkatetrayl tetra(metal), wherein the metal is Zn, Mg, B, Al, or Ga, and any carbon-containing core has from 2 to 20 carbon atoms;

R in each occurrence is a repeat unit selected from an alkadiyl metal, alkatriyl di(metal), or alkatetrayl tri(metal) having from 2 to 20 carbon atoms and a branch multiplicity of N_b;

G is the generation of the dendrimer cascade;

Z is a terminal monovalent having up to 20 carbon atoms;

N_c, is the branch multiplicity of the core; and

the shuttling agent comprises at least one generation of repeat unit R, such that G on average is a number from 2 to 150, inclusive.

6. A process for the polymerization of at least one addition polymerizable monomer to form a polymer composition, the process comprising:

contacting at least one addition polymerizable monomer with a catalyst composition under polymerization conditions;

wherein the catalyst composition comprises the contact product of at least one polymerization catalyst precursor, at least one cocatalyst, and the shuttling agent of claim 5.

7. A multiblock copolymer obtained by the process of claim 6.

8. A catalyst composition comprising the contact product at least one polymerization catalyst precursor, at least one cocatalyst, and the shuttling agent of claim 5.

9. A process for preparing the chain shuttling agent of claim 5 comprising:

a) providing a polyene having the formula $R^AC[(CH_2)_nCH=CH_2]_3$ or $C[(CH_2)_nCH=CH_2]_4$, wherein n in each occurrence is independently an integer from 0 to 20 and R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

b) contacting the polyene with a borohydride having the formula $(R^C)_2BH$, wherein R^c is a hydrocarbyl having from 1 to 20 carbon atoms, to form a first composition comprising a partially hydroborated polyene;

c) contacting the first composition with $M^A(R^{1A})_2$ or $M^B(R^{1A})_3$ to form a second composition, comprising $M^A\{CH_2CH_2(CH_2)_nE[(CH_2)_nCH=CH_2]_{m-1}\}_2$ or

$M^B\{CH_2CH_2(CH_2)_nE[(CH_2)_nCH=CH_2]_{m-1}\}_3$, wherein R^{1A} in each occurrence is independently a hydrocarbyl having from 1 to 20 carbon atoms, inclusive, optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide;

d) contacting the second composition with $(R^C)_2BH$, followed by contacting the resulting composition with $M^A(R^{1A})_2$ or $M^B(R^{1A})_3$ to form a third composition;

e) contacting the third composition with a partially hydroborated polyene prepared according to step b); and

f) repeating steps d) and e) any number of times to form a dendrimeric chain shuttling agent.

10. A process for preparing a chain shuttling agent having the formula:

$R^1[M^A\text{-}R^2\text{-}]_NM^AR^1$, wherien M^A is Zn or Mg, or

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, wherein M^B is B, Al, or Ga;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; the process comprising:

a) providing an α,ω-diene having the formula $CH_2=CH(CH_2)_nCH=CH_2$, $O[(CH_2)_nCH=CH_2]_2$, $S[(CH_2)_nCH=CH_2]_2$, $R^AN[(CH_2)_nCH=CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH=CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH=CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH=CH_2]_2O$; wherein n in each occurrence is independently an integer from 0 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive;

b) contacting the α,ω-diene with a borohydride compound having the formula $(R^C)_2BH$, wherein R^c is a hydrocarbyl having from 1 to 20 carbon atoms, to form a first composition; and

c) contacting the first composition with $M^A(R^{1A})(R^1)$ or $M^B(R^{1A})(R^1)_2$ to form a second composition comprising the chain shuttling agent;

wherein

R^{1A} in each occurrence is independently selected from hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms, inclusive, optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at

least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 2 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.

11. A chain shuttling agent having the formula:

$R^1[M^BR^1\text{-}R^2\text{-}]_NM^B(R^1)_2$, or

$M^B[R^2]_3M^B$;

or an aggregate thereof, a Lewis base-containing derivative thereof, or any combination thereof; wherein

M^B is Al;

R^1 in each occurrence is independently selected from hydrogen, halide, amide, hydrocarbyl, hydrocarbylamide, dihydrocarbylamide, hydrocarbyloxide, hydrocarbylsulfide, dihydrocarbylphosphido, tri(hydrocarbyl)silyl; any hydrocarbyl group being optionally substituted with at least one halide, amide, hydrocarbylamide, dihydrocarbylamide, or hydrocarbyloxide; and each carbon-containing R^1 having from 1 to 20 carbon atoms, inclusive;

R^2 in each occurrence is independently selected from $(CH_2)_m$, $O[(CH_2)_nCH_2CH_2]_2$, $S[(CH_2)_nCH_2CH_2]_2$, $R^AN[(CH_2)_nCH_2CH_2]_2$, $(R^B)_2Si[(CH_2)_nCH_2CH_2]_2$, $(R^B)_3SiOSiR^B[(CH_2)_nCH_2CH_2]_2$, or $[Si(R^B)_2(CH_2)_nCH_2CH_2]_2O$; wherein n in each occurrence is independently an integer from 1 to 20, inclusive; m is an integer from 3 to 20, inclusive; R^A is H or a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and R^B in each occurrence is independently a hydrocarbyl having from 1 to 12 carbon atoms, inclusive; and

N, on average, in each occurrence is a number from 2 to 150, inclusive.