anions opens an epoxide ring, one end of each polymer chain (the initiation end) is necessarily capped with a non-hydroxyl moiety such as a halogen, an alkylsulfonate, a phenylether, an acyl group, or an azide, respectively.

The other factor disfavoring the use of these catalytic systems to produce polyol resins is the fact that they produce high molecular weight polymer when taken to high conversions. Typical molecular weights are in the range of 20,000 to 400,000 g/mol—values well above the molecular weight range desired for most polyol resin applications. Potential strategies to produce lower molecular weight materials include: stopping the polymerization at low conversion; using high catalyst concentrations; degrading the high molecular weight polymer to shorter chains, or using chain transfer agents (CTAs) such as alcohols during the polymerization. Stopping the reaction at low conversion or increasing the catalyst concentration are undesirable due to cost considerations and added difficulties in purification occasioned by the increased concentration of catalyst-derived contaminants in the crude polymer. Degradation of higher molecular weight polymers to produce low molecular weight resins leads to increased polydispersity, adds additional steps to the production process, and leads to contamination with cyclic by-products. Chain transfer agents can be successfully employed to lower the molecular weight of the polymer without a significant increase in cost or contamination. However, this strategy does not alleviate the problem of non-hydroxyl end groups since polymer chains initiated by chain transfer agent will still have one end capped with a non-hydroxyl moiety (i.e. an ether corresponding to the alcohol used as the CTA).

As such, there remains a need for catalysts and methods that are capable of efficiently producing polycarbonate polyols having high carbonate content.

Summary ~~of the Invention~~

In one aspect of the present disclosure, there is provided an aliphatic polycarbonate polyol composition comprising an epoxide-CO_2 copolymer characterized in that the copolymer has:
an Mn between 400 and 20,000,
greater than 90% carbonate linkages,
and at least 98% of the end groups are hydroxyl groups.

In another aspect of the present disclosure, there is provided a polyurethane composition formed by reaction of one or more isocyanates with an aliphatic polycarbonate polyol as disclosed herein.

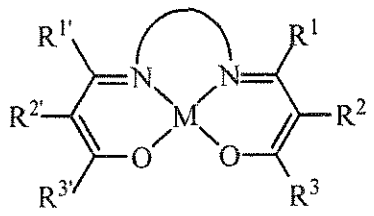
In a further aspect of the present disclosure, there is provided an article of manufacture comprising an aliphatic polycarbonate polyol composition as disclosed herein.

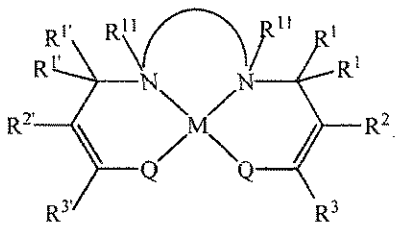
In another aspect of the present disclosure, there is provided an article of manufacture comprising the polyurethane composition as disclosed herein.

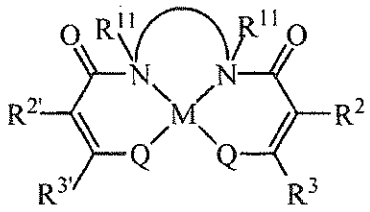
In a further aspect of the present disclosure, there is provided a polymerization formulation for the synthesis of aliphatic polycarbonate polyols having a high percentage of –OH end groups, the formulation comprising:

a metal complex having the formula L_p-M-$(L_f)_m$, where L_p is a permanent ligand set, M is a metal atom, and L_f is a ligand that is a polymerization initiator, and m is an integer between 0 and 2 inclusive representing the number of initiating ligands present;

wherein Lp-M has a formula selected from the group consisting of:



;


; and


;

wherein Q, at each occurrence is independently O or S;

R^1 and $R^{1'}$ are independently selected from the group consisting of: –H, optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; and R^{21};

R^2 and $R^{2'}$ are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; R^{14}; R^{20}; and R^{21};

R^3 and $R^{3'}$ are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle, and R^{21};

$\frown$ represents an optionally substituted moiety covalently linking two nitrogen atoms, where any of [$R^{2'}$ and $R^{3'}$], [R^2 and R^3], [R^1 and R^2], and [$R^{1'}$ and $R^{2'}$] may optionally be taken together with intervening atoms to form one or more rings which may in turn be substituted with one or more groups selected from R^{14}; R^{20}; and R^{21}; and where

R^{14} at each occurrence is independently selected from the group consisting of: halogen; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; $-OR^{10}$; $-OC(O)R^{13}$; $-OC(O)OR^{13}$; $-OC(O)NR^{11}R^{12}$; $-CN$; $-CNO$; $-C(R^{13})_zH_{(3-z)}$; $-C(O)R^{13}$; $-C(O)OR^{13}$; $-C(O)NR^{11}R^{12}$; $-NR^{11}R^{12}$; $-NR^{11}C(O)R^{13}$; $-NR^{11}C(O)OR^{13}$; $-NR^{11}SO_2R^{13}$; $-N^+R^{11}R^{12}R^{13}$ X^-; $-P^+(R^{11})_3$ X^-; $-P(R^{11})_3{=}N^+{=}P(R^{11})_3$ X^-; $-As^+R^{11}R^{12}R^{13}$ X^-; $-NCO$; $-N_3$; $-NO_2$; $-S(O)_xR^{13}$; and $-SO_2NR^{11}R^{12}$;

R^{20} at each occurrence is independently selected from the group consisting of: halogen; $-OR^{10}$; $-OC(O)R^{13}$; $-OC(O)OR^{13}$; $-N^+(R^{11})_3$ X^-; $-P^+(R^{11})_3$ X^-; $-P(R^{11})_3{=}N^+{=}P(R^{11})_3$ X^-; $-As^+R^{11}R^{12}R^{13}$ X^-; $-OC(O)NR^{11}R^{12}$; $-CN$; $-CNO$; $-C(O)R^{13}$; $-C(O)OR^{13}$; $-C(O)NR^{11}R^{12}$; $-C(R^{13})_zH_{(3-z)}$; $-NR^{11}R^{12}$; $-NR^{11}C(O)R^{13}$; $-NR^{11}C(O)OR^{13}$; $-NCO$; $-NR^{11}SO_2R^{13}$; $-S(O)_xR^{13}$; $-S(O)_2NR^{11}R^{12}$; $-NO_2$; $-N_3$; and $-Si(R^{13})_{(3-z)}[(CH_2)_kR^{14}]_z$;

R^{21} at each occurrence is independently selected from the group consisting of: $-(CH_2)_kR^{20}$; $-(CH_2)_k$-Z"-$(CH_2)_kR^{20}$; $-C(R^{17})_zH_{(3-z)}$; $-(CH_2)_kC(R^{17})_zH_{(3-z)}$; $-(CH_2)_m$-Z"-$(CH_2)_mC(R^{17})_zH_{(3-z)}$; $-(CH_2)_k$-Z"-R^{16};

X^- is any anion,

Z" is a divalent linker selected from the group consisting of -$(CH{=}CH)_a$-; -$(CH{\equiv}CH)_a$-; -C(O)-; -C(=NOR^{11})-; -C(=$NNR^{11}R^{12}$)-; –O–; –OC(O)–; -C(O)O-; -OC(O)O-; -$N(R^{11})$-; -N(C(O)R^{13})-; -C(O)NR^{13}-; -N(C(O)R^{13})O-; -NR^{13}C(O)R^{13}N-; -$S(O)_x$-; a polyether; and a polyamine.

R^{10} at each occurrence is independently selected from the group consisting of: –H; optionally substituted C_{1-12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14-membered heterocycle $–S(O)_2R^{13}$; $–Si(R^{15})_3$; $–C(O)R^{13}$; and a hydroxyl protecting group,

R^{11} and R^{12} at each occurrence are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14-membered heterocycle; where two or more R^{11} or R^{12} groups can optionally be taken together with intervening atoms to form an optionally substituted 3- to 10-membered ring,

R^{13} at each occurrence is independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; and optionally substituted 3- to 14-membered heterocycle, where two or more R^{13} groups on the same molecule may optionally be taken together to form ring.

R^{15} at each occurrence is independently selected from the group consisting of: optionally substituted C_{1-12} aliphatic, an optionally substituted 3- to 14-membered carbocycle; and an optionally substituted 3- to 14-membered heterocycle,

a is 1, 2, 3, or 4,

k is independently at each occurrence an integer from 1 to 8, inclusive,

m is 0 or an integer from 1 to 8, inclusive,

x is 0, 1, or 2, and

z is 1, 2, or 3;

and

a chain transfer agent having a plurality of sites capable of initiating copolymerization of epoxides and CO_2; wherein the chain transfer agent and metal complex are present in a molar ratio ranging from 50:1 to 500:1, 500:1 to 1000:1, or greater than 1000:1;

wherein the chain transfer agent has a structure $Y\text{-}A\text{-}(Y)_n$,

where:

each –Y group is independently a functional group capable of initiating chain growth of epoxide CO_2 copolymers and each Y group may be the same or different;

-A- is a covalent bond or a multivalent moiety; and

n is an integer between 1 and 10, inclusive;

wherein said aliphatic polycarbonate polyols have an average molecular weight number between 400 g/mol and 20,000 g/mol, and at least 98% of the end groups are hydroxyl groups.

In another aspect of the present disclosure, there is provided a method for the synthesis of aliphatic polycarbonate polyols having a high percentage of –OH end groups, the method comprising the steps of:

a) contacting a reaction mixture comprising one or more epoxides with a polymerization formulation of claim 43 in the presence of carbon dioxide, wherein the molar ratio of metal complex to epoxide ranges from 1:100 to 1:1,000,000;

b) allowing the polymerization reaction to proceed until a desired molecular weight aliphatic polycarbonate polyol has formed, wherein in the aliphatic polycarbonate polyol composition, at least 98% of the end groups are hydroxyl groups, and wherein the polycarbonate polyol has an average molecular weight number between 400 and 20,000; and

c) terminating the polymerization.

~~In one aspect,~~ The present disclosure encompasses polymerization systems for the copolymerization of CO_2 and epoxides comprising 1) a metal complex including a metal coordination compound having a permanent ligand set and at least one ligand that is a polymerization initiator, and 2) a chain transfer agent having two or more sites that can initiate polymerization.

features: a carbonate-to-ether linkage ratio of at least 10:1, a head-to-tail ratio of at least 5:1, or a polydispersity index of less than 2. In certain embodiments ~~of this aspect~~, a polymer composition is further characterized in that a polymer contains a plurality of polymer chain types differentiated by the presence of different polyfunctional polymerization initiators embedded within the chain, or by differences in the end-groups present on the polymer chains.

In certain embodiments, polycarbonate polyol compositions of the present disclosure are further characterized in that they contain a mixture of two or more chain types, wherein the chain different chain types are differentiated from one another by differences in the identity of the embedded polyfunctional polymerization initiators, the absence of embedded polyfunctional polymerization initiators, or the presence of non-hydroxyl end groups on certain chains.

Definitions

Definitions of specific functional groups and chemical terms are described in more detail below. For purposes of this invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 75th Ed., inside cover, and specific functional groups are generally defined as described therein. Additionally, general principles of organic chemistry, as well as specific functional moieties and reactivity, are described in *Organic Chemistry*, Thomas Sorrell, University Science Books, Sausalito, 1999; Smith and March *March's Advanced Organic Chemistry*, 5th Edition, John Wiley & Sons, Inc., New York, 2001; Larock, *Comprehensive Organic Transformations*, VCH Publishers, Inc., New York, 1989; Carruthers, *Some Modern Methods of Organic Synthesis*, 3rd Edition, Cambridge University Press, Cambridge, 1987; the entire contents of each of which are incorporated herein by reference.

Certain compounds of the present invention can comprise one or more asymmetric centers, and thus can exist in various stereoisomeric forms, *e.g.*, enantiomers and/or diastereomers. Thus, inventive compounds and compositions thereof may be in the form of an individual enantiomer, diastereomer or geometric isomer, or may be in the form of a

CLAIMS

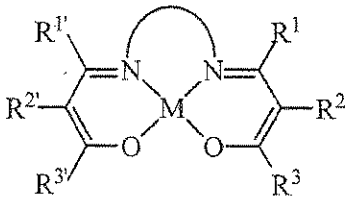
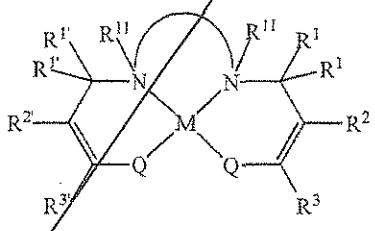
What is claimed is:

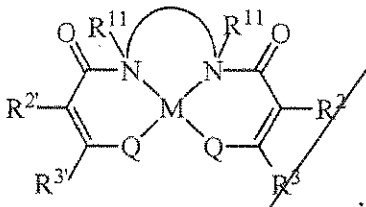
1. A polymerization system for the copolymerization of CO_2 and epoxides, the system comprising:

a metal complex having the formula L_p-M-$(L_l)_m$, where L_p is a permanent ligand set, M is a metal atom, L_l is a ligand that is a polymerization initiator, and m is an integer between 0 and 2, inclusive representing the number of initiating ligands present; and

a chain transfer agent having a plurality of sites capable of initiating copolymerization of epoxides and CO_2;

wherein L_p-M has a formula selected from the group consisting of:



; ; and


;

wherein:

Q, at each occurrence is independently O or S;

R^1 and $R^{1'}$ are independently selected from the group consisting of: –H, optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; and R^{21};

R^2 and $R^{2'}$ are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; R^{14}; R^{20}; and R^{21};

R^3, and $R^{3'}$ are independently selected from the group consisting of:

–H; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle, and R^{21};

⌒ represents an optionally substituted moiety covalently linking two nitrogen atoms,

where any of [$R^{2'}$ and $R^{3'}$], [R^2 and R^3], [R^1 and R^2], and [$R^{1'}$ and $R^{2'}$] may optionally be taken together with intervening atoms to form one or more rings which may in turn be substituted with one or more groups selected from R^{14}; R^{20}; and R^{21}; and where

R^{14} at each occurrence is independently selected from the group consisting of: halogen; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; –OR^{10}; –$OC(O)R^{13}$; –$OC(O)OR^{13}$;–$OC(O)NR^{11}R^{12}$; –CN; –CNO; –$C(R^{13})_zH_{(3-z)}$; –$C(O)R^{13}$; –$C(O)OR^{13}$; –$C(O)NR^{11}R^{12}$; –$NR^{11}R^{12}$; –$NR^{11}C(O)R^{13}$; –$NR^{11}C(O)OR^{13}$; –$NR^{11}SO_2R^{13}$; –$N^+R^{11}R^{12}R^{13}$ X^-; –$P^+(R^{11})_3$ X^-; –$P(R^{11})_3{=}N^+{=}P(R^{11})_3$ X^-; –$As^+R^{11}R^{12}R^{13}$ X^-; –NCO; –N_3; –NO_2; –$S(O)_xR^{13}$; and –$SO_2NR^{11}R^{12}$,

R^{20} at each occurrence is independently selected from the group consisting of: halogen; –OR^{10}; –$OC(O)R^{13}$; –$OC(O)OR^{13}$; –$N^+(R^{11})_3$ X^-; –$P^+(R^{11})_3$ X^-; –$P(R^{11})_3{=}N^+{=}P(R^{11})_3$ X^-; –$As^+R^{11}R^{12}R^{13}$ X^-; –$OC(O)NR^{11}R^{12}$; –CN; –CNO; –$C(O)R^{13}$; –$C(O)OR^{13}$; –$C(O)NR^{11}R^{12}$; –$C(R^{13})_zH_{(3-z)}$; –$NR^{11}R^{12}$; –$NR^{11}C(O)R^{13}$; –$NR^{11}C(O)OR^{13}$; –NCO; –$NR^{11}SO_2R^{13}$; –$S(O)_xR^{13}$; –$S(O)_2NR^{11}R^{12}$; –NO_2; –N_3; and –$Si(R^{13})_{(3-z)}[(CH_2)_kR^{14}]_z$,

R^{21} at each occurrence is independently selected from the group consisting of: –$(CH_2)_kR^{20}$; –$(CH_2)_k$-Z-$(CH_2)_kR^{20}$; –$C(R^{17})_zH_{(3-z)}$; –$(CH_2)_kC(R^{17})_zH_{(3-z)}$; –$(CH_2)_m$-Z-$(CH_2)_mC(R^{17})_zH_{(3-z)}$; –$(CH_2)_k$-Z-$R^{16}$;

X^- is any anion,

Z is a divalent linker selected from the group consisting of -$(CH{=}CH)_a$-; -$(CH{\equiv}CH)_a$-; -C(O)-; -C(=NOR^{11})-; -C(=$NNR^{11}R^{12}$)-; -O–; –OC(O)–; -C(O)O-; -OC(O)O-; -$N(R^{11})$-; -$N(C(O)R^{13})$-; -$C(O)NR^{13}$-; -$N(C(O)R^{13})$O-; -$NR^{13}C(O)R^{13}$N-; -$S(O)_x$-; a polyether; and a polyamine,

R^{10} at each occurrence is independently selected from the group consisting of:

–H; optionally substituted C_{1-12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14-membered heterocycle $–S(O)_2R^{13}$; $–Si(R^{15})_3$; $–C(O)R^{13}$; and a hydroxyl protecting group,

R^{11} and R^{12} at each occurrence are independently selected from the group consisting of:

–H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14-membered heterocycle; where two or more R^{11} or R^{12} groups can optionally be taken together with intervening atoms to form an optionally substituted 3- to 10-membered ring,

R^{13} at each occurrence is independently selected from the group consisting of:

–H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; and optionally substituted 3- to 14-membered heterocycle, where two or more R^{13} groups on the same molecule may optionally be taken together to form ring,

R^{15} at each occurrence is independently selected from the group consisting of:

optionally substituted C_{1-12} aliphatic, an optionally substituted 3- to 14-membered carbocycle; and an optionally substituted 3- to 14-membered heterocycle,

a is 1, 2, 3, or 4,

k is independently at each occurrence an integer from 1 to 8 inclusive,

m is 0 or an integer from 1 to 8 inclusive,

x is 0, 1, or 2, and

z is 1, 2, or 3;

wherein the chain transfer agent has a structure Y-A-$(Y)_n$,

where:

each –Y group is independently a functional group capable of initiating chain growth of epoxide CO_2 copolymers and each Y group may be the same or different;

-A- is a covalent bond or a multivalent moiety; and

n is an integer between 1 and 10, inclusive.

2. The polymerization system of claim 1, wherein each Y group is independently selected from the group consisting
of: -OH, -C(O)OH, -C(OR^y)OH, -OC(R^y)OH, -NHR^y, -NHC(O)R^y, -NHC=NR^y; -NR^yC=NH; -NR^yC(NR^y_2)=NH; -NHC(NR^y_2)=NR^y; -NHC(O)OR^y, -NHC(O)NR^y_2; -C(O)NHR^y, -C(S)NHR^y, -OC(O)NHR^y, -OC(S)NHR^y, -SH, -C(O)SH, -B(OR^y)OH, -$P(O)_a(R^y)_b(OR^y)_c(O)_dH$, -$OP(O)_a(R^y)_b(OR^y)_c(O)_dH$, –$N(R^y)$OH, -ON($R^y$)H; =NOH, =NN($R^y$)H, where each occurrence of R^y is independently –H, or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic, C_{1-20} heteroaliphatic, 3- to 12-membered heterocyclic, and 6- to 12-membered aryl, *a* and *b* are each independently 0 or 1, *c* is 0, 1 or 2, *d* is 0 or 1, and the sum of *a*, *b*, and *c* is 1 or 2 and where an acidic hydrogen atom bound in any of the above functional groups may be replaced by a metal atom or an organic cation.

3. The polymerization system of claim 1, wherein each Y group is independently selected from the group consisting of: -OH, and -C(O)OH.

4. The polymerization system of claim 1, wherein –A- is an optionally substituted radical selected from the group consisting of: C_{2-30} aliphatic, C_{2-30} heteroaliphatic, 6- to 12-membered aryl, 3- to 12-membered heterocyclic, 5- to 12-membered heteroaryl, polyolefins, polyesters, polyethers, polycarbonates, polyoxymethylene and mixtures of two or more of these.

5. The polymerization system of claim 1, wherein *n* is 1 to 4.

6. The polymerization system of claim 1, wherein *n* is 1.

7. The polymerization system of claim 1, wherein *n* is 2.

8. The polymerization system of claim 1, wherein *n* is 3.

9. The polymerization system of claim 1, wherein the chain transfer agent is a polyhydric alcohol.

10. The polymerization system of claim 1, wherein the chain transfer agent is a diol.

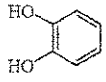
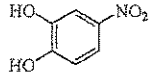
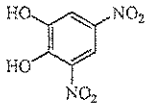
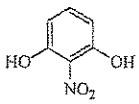
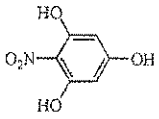
11. The polymerization system of claim 1, wherein the chain transfer agent is selected from the group consisting of: 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethylpropane-1,3-diol, 2-butyl-2-ethylpropane-1,3-diol, 1,5-hexanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 2,2,4,4-tetramethylcyclobutane-1,3-diol, 1,3-cyclopentanediol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4- cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, and 1,4-cyclohexanediethanol.

12. The polymerization system of claim 1, wherein the chain transfer agent is selected from the group consisting of: diethylene glycol, triethylene glycol, tetraethylene glycol, higher poly(ethylene glycol), preferrably those having number average molecular weights of from 220 to about 2000 g/mol, dipropylene glycol, tripropylene glycol, and higher poly(propylene glycols) preferrably those having number average molecular weights of from 234 to about 2000 g/mol.

13. The polymerization system of claim 1, wherein the chain transfer agent is selected from the group consisting of: 4,4'-(1-methylethylidene) bis[cyclohexanol], 2,2'-methylenebis[phenol], 4,4'-methylenebis[phenol], 4,4'-(phenylmethylene)bis[phenol], 4,4'-(diphenylmethylene)bis[phenol], 4,4'-(1,2-ethanediyl)bis[phenol], 4,4'-(1,2-cyclohexanediyl)bis[phenol], 4,4'-(1,3-cyclohexanediyl)bis[phenol], 4,4'-(1,4-cyclohexanediyl)bis[phenol], 4,4'-ethylidenebis[phenol], 4,4'-(1-phenylethylidene)bis[phenol], 4,4'-propylidenebis[phenol], 4,4'-cyclohexylidenebis [phenol], 4,4'-(1-methylethylidene)bis[phenol], 4,4'-(1-methylpropylidene)bis[phenol], 4,4'-(1-ethylpropylidene)bis[phenol], 4,4'-cyclohexylidenebis[phenol], 4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyldi-2, 1- ethanediyl)bis[phenol], 1,2-benzenedimethanol, 1,3-benzenedimethanol, 1,4-benzenedimethanol, 4,4'-[1,3-phenylenebis(1-

methylethylidene)]bis[phenol], 4,4'-[1,4-phenylenebis(1-methylethylidene)]bis[phenol], phenolphthalein, 4,4'-(1-methylidene)bis[2-methylphenol], 4,4'-(1-methylethylidene)bis[2-(1-methylethyl)phenol], and 2,2'-methylenebis[4-methyl-6-(1-methylethyl)phenol].

14. The polymerization system of claim 1, wherein the chain transfer agent is selected from the group consisting of:


; 
; 
; 
; and .

15. The polymerization system of claim 1, wherein the chain transfer agent is selected from the group consisting of: 1,3 propane diol, 1,4 butane diol, dipropylene glycol, diethylene glycol, and isosorbide.

16. The polymerization system of claim 1, wherein the chain transfer agent is a hydroxy acid.

17. The polymerization system of claim 16, wherein the hydroxy acid is an alpha-hydroxy acid.

18. The polymerization system of claim 17, wherein the hydroxy acid is selected from the group consisting of: glycolic acid, DL-lactic acid, D-lactic acid, L-lactic, citric acid and mandelic acid.

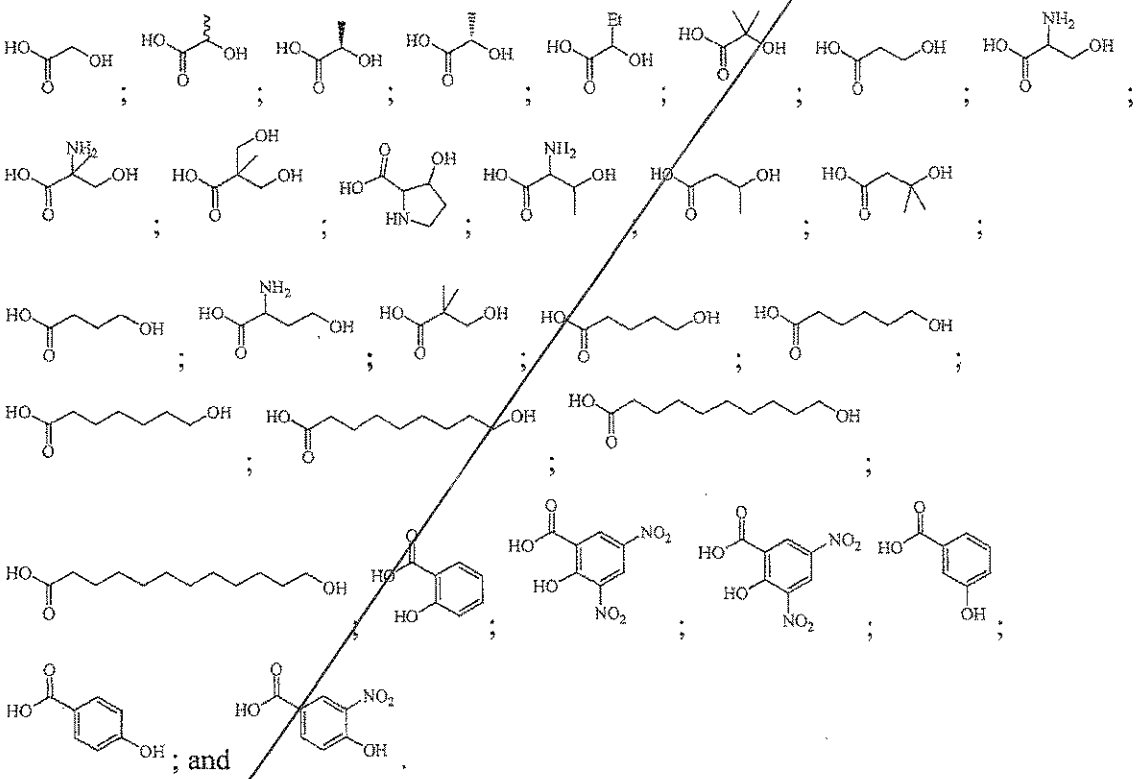
19. The polymerization system of claim 16, wherein the hydroxy acid is a beta-hydroxy acid.

20. The polymerization system of claim 19, wherein the hydroxy acid is selected from the group consisting of: 3-hydroxypropionic acid, DL 3-hydroxybutryic acid, D-3 hydroxybutryic acid, L 3-hydroxybutyric acid, DL-3-hydroxy valeric acid, D-3-hydroxy valeric acid, L-3-hydroxy valeric acid, salicylic acid, and derivatives of salicylic acid.

21. The polymerization system of claim 16, wherein the hydroxy acid is a α-ω hydroxy acid.

22. The polymerization system of claim 16, wherein the hydroxy acid is selected from the group consisting of: of optionally substituted C_{3-20} aliphatic α-ω hydroxy acids and polyester oligomeric esters.

23. The polymerization system of claim 16, wherein the hydroxy acid is selected from the group consisting of:

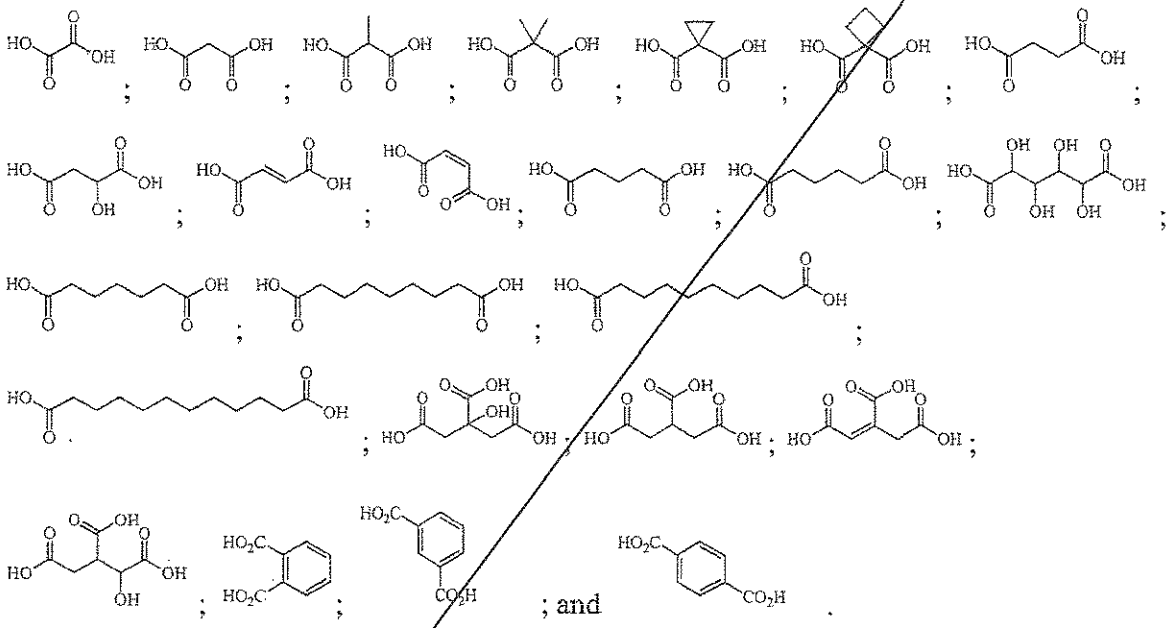

; and

24. The polymerization system of claim 1, wherein the chain transfer agent is a polycarboxylic acid.

25. The polymerization system of claim 1, wherein the chain transfer agent is diacid.

26. The polymerization system of claim 25, wherein the chain transfer agent is selected from the group consisting of: phthalic acid, isophthalic acid, terephthalic acid, maleic acid, succinic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, and azelaic acid.

27. The polymerization system of claim 1, wherein the chain transfer agent is selected from the group consisting of:


; and

28. The polymerization system of claim 1, wherein M is selected from periodic table groups 3-13, inclusive.

29. The polymerization system of claim 1, wherein M is selected from periodic table groups 5-12, inclusive.

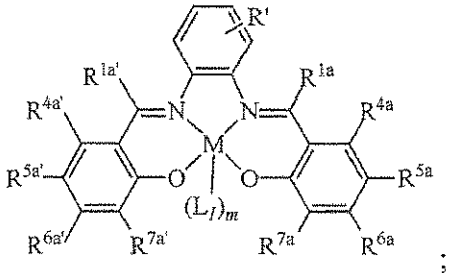
30. The polymerization system of claim 1, wherein M is selected from the group consisting of Cr, Mn, V, Fe, Co, Mo, W, Ru, Al, and Ni.

31. The polymerization system of claim 1, wherein M is Cr.

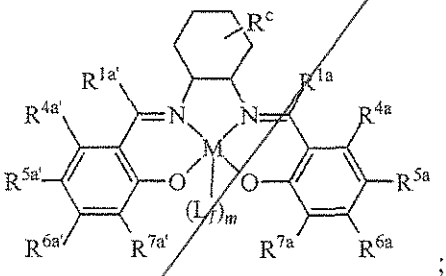
32. The polymerization system of claim 1, wherein M is Mn.

33. The polymerization system of claim 1, wherein M is Co.

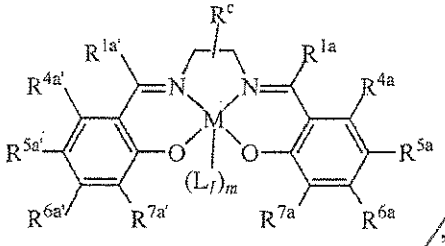
34. The polymerization system of claim 1, wherein L_p-M-$(L_f)_m$ has a formula selected from the group consisting of:



;



; and



,

wherein:

R^c at each occurrence is independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14 membered heterocycle; R^{20}; and R^{21}, where two or more R^c groups may be taken together with intervening atoms to form one or more optionally substituted rings and, when two R^c groups are attached to the same carbon atom, they may be taken together along with the carbon atom to which they are attached to form a moiety selected from the group consisting of: an optionally substituted 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, and an imine;

R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, $R^{6a'}$, R^{7a}, and $R^{7a'}$ are each independently hydrogen, a $\sim\sim(Z)_p$ group,

halogen, $-NO_2$, -CN, $-SR^{13}$, $-S(O)R^{13}$, $-S(O)_2R^{13}$, $-NR^{11}C(O)R^{13}$, $-OC(O)R^{13}$, $-CO_2R^{13}$, -NCO, $-N_3$, $-OR^{10}$, $-OC(O)NR^{11}R^{12}$, $-Si(R^{13})_3$, $-NR^{11}R^{12}$, $-NR^{11}C(O)R^{13}$, and $-NR^{11}C(O)OR^{13}$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; 6- to 10-membered aryl; 5- to 10-membered heteroaryl; and 3- to 7-membered heterocyclic, where [R^{4a} and R^{4a}], [$R^{1a'}$ and $R^{4a'}$] and any two adjacent R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, $R^{6a'}$, R^{7a}, and $R^{7a'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms;

R^{1a} and $R^{1a'}$ are hydrogen when not taken together with R^{4a} and $R^{4a'}$;

R′ is R^d or a $\sim\sim(Z)_p$ group, where two or more adjacent R′ groups can be taken together to form an optionally substituted saturated, partially unsaturated, or aromatic 3- to 12-membered ring containing 0 to 4 heteroatoms;

R^d is selected from the group consisting of: optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; R^{20}; and R^{21};

n is 0 or an integer from 1 to 8, inclusive;

p is 0 or an integer from 1 to 4, inclusive; and

where a $\sim\sim(Z)_p$ group comprises a covalent linker "$\sim\sim$" containing one or more atoms selected from the group consisting of C, O, N, S, and Si; "Z" is an activating functional group having co-catalytic activity in epoxide CO_2 copolymerization, and *p* is an integer from 1 to 4 indicating the number of individual activating functional groups Z present on a given $\sim\sim(Z)_p$ group.

35. The polymerization system of claim 34, wherein R^{1a}, $R^{1a'}$, R^{4a}, $R^{4a'}$, R^{6a}, and $R^{6a'}$ are each -H.

36. The polymerization system of claim 34, wherein R^{5a}, $R^{5a'}$, R^{7a} and $R^{7a'}$ are each optionally substituted C_1-C_{12} aliphatic.

37. The polymerization system of claim 34, wherein R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, $R^{6a'}$, R^{7a}, and $R^{7a'}$ are each independently selected from the group consisting of: -H, $-SiR_3$; methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *sec*-butyl, *t*-butyl, isoamyl, *t*-amyl, thexyl, and trityl.

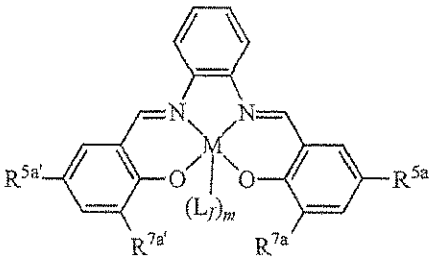
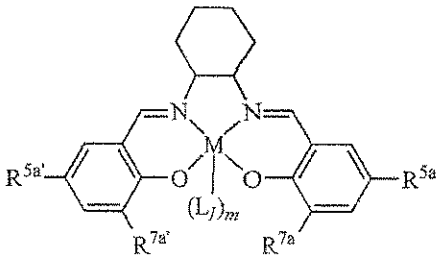
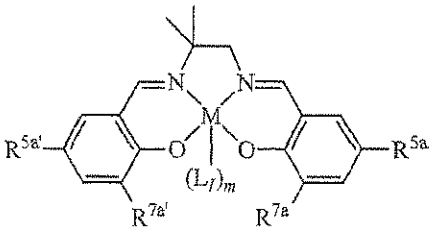
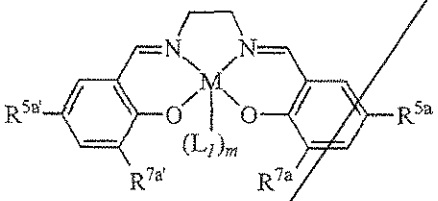
38. The polymerization system of claim 34, wherein R^{7a} is selected from the group consisting of -H; methyl; ethyl; *n*-propyl; *i*-propyl; *n*-butyl; *sec*-butyl; *t*-butyl; isoamyl; *t*-amyl; thexyl; and trityl.

39. The polymerization system of claim 34, wherein one or more of R^{5a}, $R^{5a'}$, R^{7a} and $R^{7a'}$ is a $\sim\!\!\sim(Z)_p$ group.

40. The polymerization system of claim 34, wherein R^{5a} and $R^{5a'}$ are each a $\sim\!\!\sim(Z)_p$ group.

41. The polymerization system of claim 34, wherein R^{5a} is a $\sim\!\!\sim(Z)_p$ group and $R^{5a'}$ is $C_{1\text{-}8}$ aliphatic.

42. The polymerization system of claim 34, wherein L_p-M-$(L_l)_m$ has a formula selected from the group consisting of:



;
;


; and

43. The polymerization system of claim 42, wherein -M- is cobalt.

44. The polymerization system of claim 1, wherein the initiating ligand (L_I) is any anion.

45. The polymerization system of claim 1, wherein the initiating ligand (L_I) is selected from the group consisting of: azide, halides, alkyl sulfonates, carboxylates, alkoxides, and phenolates.

46. The polymerization system of claim 1, wherein the initiating ligand (L_I) is selected from the group consisting of: $-OR^x$, $-SR^x$, $-OC(O)R^x$, $-OC(O)OR^x$, $-OC(O)N(R^x)_2$, $-NR^xC(O)R^x$, -CN, halo (*e.g.*, -Br, -I, -Cl), $-N_3$, and $-OSO_2R^x$ wherein each R^x is, independently, selected from hydrogen, optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted aryl and optionally substituted heteroaryl and where two Rx groups can be taken together to form an optionally substituted ring optionally containing one or more additional heteroatoms.

47. The polymerization system of claim 1, wherein the initiating ligand (L_I) is $-OC(O)R^x$, wherein R^x is selected from optionally substituted aliphatic, fluorinated aliphatic, optionally

substituted heteroaliphatic, optionally substituted aryl, fluorinated aryl, and optionally substituted heteroaryl.

48. The polymerization system of claim 1, wherein the initiating ligand (L_I) comprises a compound of the formula $-Q'\text{-}A'(Z')_n$, wherein:

–Q'- is a carboxy or alkoxy group,

-A'- is a multivalent moiety,

each Z' is independently a functional group that can initiate a polymer chain, and

n is an integer between 1 and 10 inclusive.

49. The polymerization system of claim 1, wherein the ligand that is a polymerization initiator and the chain transfer agent are the same compound or ionic forms of the same molecule.

50. The polymerization system of claim 1, wherein the chain transfer agent is present in a molar ratio of at least 10:1 relative to the metal complex.

51. The polymerization system of claim 1, wherein the chain transfer agent is present in a molar ratio of between about 10:1 and about 1000:1 relative to the metal complex.

52. The polymerization system of claim 1, wherein the chain transfer agent is present in a molar ratio of between about 50:1 and about 500:1 relative to the metal complex.

53. The polymerization system of claim 1, wherein the chain transfer agent is present in a molar ratio of between about 50:1 and about 250:1 relative to the metal complex.

54. The polymerization system of claim 1, wherein the chain transfer agent is present in a molar ratio of between about 20:1 and about 100:1 relative to the metal complex.

55. The polymerization system of claim 1, wherein the chain transfer agent is present in a molar ratio of between about 100:1 and about 250:1 relative to the metal complex.

56. The polymerization system of claim 1, further comprising a co-catalyst.

57. The polymerization system of claim 56, wherein the co-catalyst is selected from the group consisting of: amines, guanidines, amidines, phosphines, nitrogen-containing heterocycles, ammonium salts, phosphonium salts, arsonium salts, bisphosphine ammonium salts, and a combination of any two or more of these.

58. The polymerization system of claim 56, wherein the co-catalyst comprises an 'onium' salt.

59. The polymerization system of claim 58, wherein the 'onium' salt includes a counterion that is a polyfunctional polymerization initiator.

60. The polymerization system of claim 59, wherein the counterion that is a polyfunctional polymerization initiator and the chain transfer agent are the same compound, or ionic forms of the same compound.

61. The polymerization system of claim 59, wherein the counterion that is a polyfunctional polymerization initiator and the chain transfer agent and the ligand that is a polymerization initiator are the same compound, or ionic forms of the same compound.

62. The polymerization system of claim 56, wherein the co-catalyst is present in a molar ratio of from about 0.1:1 to about 10:1 relative to the metal complex.

63. The polymerization system of claim 56, wherein the co-catalyst is present in a molar ratio of from about 0.5:1 to about 5:1 relative to the metal complex.

64. The polymerization system of claim 56, wherein the co-catalyst is present in a molar ratio of from about 1:1 to about 4:1 relative to the metal complex.

65. The polymerization system of claim 56, wherein the co-catalyst is present in a molar ratio of about 1:1 relative to the metal complex.

66. The polymerization system of claim 56, wherein the co-catalyst is present in a molar ratio of about 2:1 relative to the metal complex.

67. A method for the synthesis of aliphatic polycarbonate polyols having a high percentage of –OH end groups, the method comprising the steps of:

a) contacting a reaction mixture comprising one or more epoxides with a polymerization system of any of claims 1-66 in the presence of carbon dioxide;

b) allowing the polymerization reaction to proceed until a desired molecular weight aliphatic polycarbonate polyol has formed, and

c) terminating the polymerization.

68. The method of claim 67, wherein at least 50% of epoxide in the reaction mixture is converted to aliphatic polycarbonate polyol.

69. The method of claim 67, wherein the molar ratio of chain transfer agent to metal complex is between about 10:1 and 1,000:1.

70. The method of claim 67, wherein the molar ratio of chain transfer agent to metal complex is between about 40:1 and 400:1.

71. The method of claim 67, wherein at least 90% of the end groups of the polycarbonate polyol formed are OH groups.

72. The method of claim 67, wherein at least 95% of the end groups of the polycarbonate polyol formed are OH groups.

73. The method of claim 67, wherein at least 97% of the end groups of the polycarbonate polyol formed are OH groups.

74. The method of claim 67, wherein at least 98% of the end groups of the polycarbonate polyol formed are OH groups.

75. The method of claim 67, wherein at least 99% of the end groups of the polycarbonate polyol formed are OH groups.

76. The method of claim 67, wherein the PDI of the polycarbonate polyol formed is less than 1.6.

77. The method of claim 67, wherein the PDI of the polycarbonate polyol formed is less than 1.2.

78. The method of claim 67, wherein more than 80% of the linkages formed by the metal complex are carbonate linkages.

79. The method of claim 67, wherein more than 90% of the linkages formed by the metal complex are carbonate linkages.

80. The method of claim 67, wherein more than 95% of the linkages formed by the metal complex are carbonate linkages.

81. The method of claim 67, wherein the polycarbonate polyol has an average molecular weight number between about 300 g/mol and about 20,000 g/mol.

82. The method of claim 67, wherein the epoxide comprises propylene oxide.

83. The method of claim 82, wherein the head-to-tail ratio of the polycarbonate polyol is greater than 80%.

84. The method of claim 82, wherein the head-to-tail ratio of the polycarbonate polyol is greater than 90%.

85. The method of claim 82, wherein the head-to-tail ratio of the polycarbonate polyol is greater than 95%.

86. The method of claim 67, wherein less than about 5% cyclic carbonate is formed.

87. The method of claim 67, wherein the chain transfer agent is selected from the group consisting of: water; polyhydric alcohols; polyacids; hydroxy acids; primary amines; polyamines, amino alcohols, amino acids, aldehyde hydrates, ketone hydrates, formaldehyde, polyhydric thiols, hydroxy thiols, amino thiols, and mercapto acids, boronic acids, and mixtures of any two or more of these.

88. The method of claim 67, wherein the chain transfer agent is selected from the group consisting of: water; polyhydric alcohols; polyacids; and hydroxy acids, and mixtures of any two or more of these.

89. The method of claim 67, further comprising the step of calculating a molar ratio of chain transfer agent relative to metal complex to be used in the polymerization, the calculation comprising the substeps of: i) selecting a desired length of time for which the polymerization reaction is to be run, ii) multiplying the selected length of time for which the polymerization reaction is to run by the turnover frequency of the metal complex under the reaction conditions iii) multiplying this result by the desired mol% conversion of epoxide, and iv) using the inverse of this result as the ratio of metal complex to epoxide used for the reaction.

90. The method of claim 89, further comprising the step of calculating the ratio of chain transfer agent to polymerization metal complex to used in the polymerization, calculation comprising the substeps of; v) taking the value from step (iii) and multiplying this result by the molecular weight of the repeating unit of the polycarbonate; vi) selecting a desired molecular weight for the polyol and dividing the result from step (v) by this number; and vii) subtracting the number of chains produced per metal complex molecule from the result of step (vi) and taking the result as the ratio of chain transfer agent to metal complex used in step (a).

91. The method of claim 67, further comprising the steps of measuring the amount of water present in the reaction mixture and reducing the amount of chain transfer agent added to the reaction mixture by an amount determined by the result of the water measurement.

92. The method of claim 67, further comprising the step of drying the reaction mixture prior to step (b).

93. The method of claim 67, further comprising the steps of measuring the molecular weight of the polymer formed in the reaction mixture at two or more time points, extrapolating the time at which a desired molecular weight of polymer will have formed, and terminating the polymerization reaction at the extrapolated time.

94. The method of claim 93, wherein the molecular weight of the polymer is determined by gel permeation chromatography.

95. A polycarbonate polyol composition comprising an epoxide CO_2 copolymer characterized in that the copolymer has:
an Mn between about 400 and about 20,000,
greater than 90% carbonate linkages, and
at least 90% of the end groups are hydroxyl groups.

96. The polycarbonate polyol composition of claim 95, comprising greater than 92% carbonate linkages.

97. The polycarbonate polyol composition of claim 95, comprising greater than 95% carbonate linkages.

98. The polycarbonate polyol composition of claim 95, comprising greater than 97% carbonate linkages.

99. The polycarbonate polyol composition of claim 95, comprising greater than 99% carbonate linkages.

100. The polycarbonate polyol composition of claim 95, having an Mn between about 500 and about 5,000 g/mol.

101. The polycarbonate polyol composition of claim 95, having an Mn between about 800 and about 4,000 g/mol.

102. The polycarbonate polyol composition of claim 95, having an Mn between about 1,000 and about 3,000 g/mol.

103. The polycarbonate polyol composition of claim 95, having an Mn of about 1,000 g/mol.

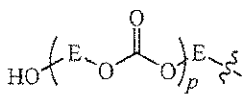
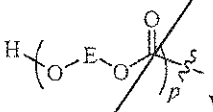
104. The polycarbonate polyol composition of claim 95, having an Mn of about 2,000 g/mol.

105. The polycarbonate polyol composition of claim 95, having an Mn of about 4,000 g/mol.

106. The polycarbonate polyol composition of claim 95, having an Mn of about 8,000 g/mol.

107. The polycarbonate polyol composition of claim 95 comprising polymer chains denoted P^1 having the formula T-Y-A-(Y-T)$_n$ wherein:

each -T is a polycarbonate chain having a formula independently selected from the group consisting of:

 and  wherein:

E is an optionally substituted C_2 unit derived from an epoxide, where E may represent a monomer unit derived from one type of epoxide, or a mixture of two or more types of epoxide, and

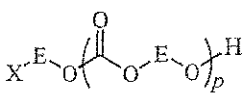
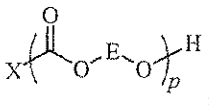
p ranges from about 5 to about 10,000

each –Y group is independently a functional group capable of initiating chain growth of epoxide CO_2 copolymers and each Y group may be the same or different,

-A- is a covalent bond or a multivalent moiety; and

n is an integer between 1 and 10 inclusive.

108. The polycarbonate polyol composition of claim 107, further comprising polymer chains denoted P^2 having a formula selected from the group consisting of:

 and , wherein

X is a bound form of an anion capable of initiating only one polymer chain.

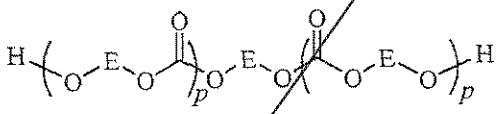
109. The polycarbonate polyol composition of claim 108 wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 9:1.

110. The polycarbonate polyol composition of claim 108 wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 20:1.

111. The polycarbonate polyol composition of claim 108 wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 40:1.

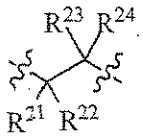
112. The polycarbonate polyol composition of claim 108 wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 100:1.

113. The polycarbonate polyol composition of any of claims 107-112, further comprising polymer chains denoted P^{1a} having a formula:



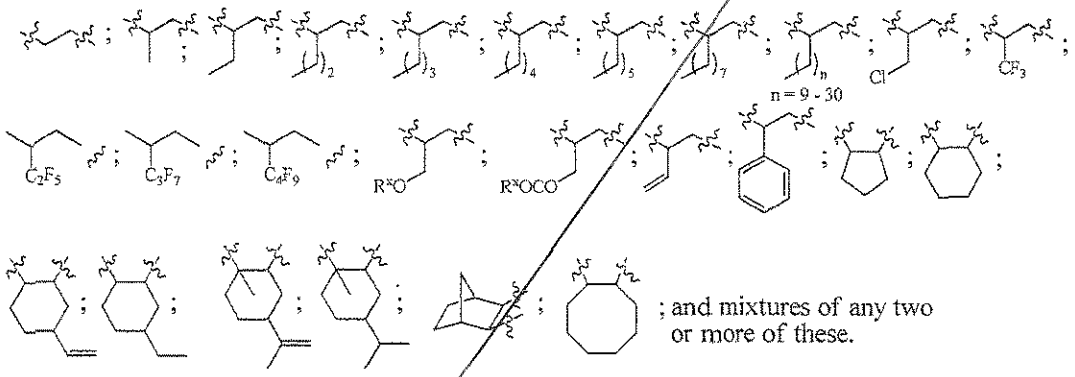
114. The polycarbonate polyol composition of any of claim 113 wherein the ratio of P^1 polymer chains to P^{1a} polymer chains is greater than 20:1.

115. The polycarbonate polyol composition of any of claims 107-112, wherein each E is



, where, R^{21}, R^{22}, R^{23}, and R^{24}, are each independently selected from the group consisting of: –H; and an optionally substituted group selected from C_{1-30} aliphatic; C_{6-14} aryl; 3- to 12-membered heterocycle, and 5- to 12-membered heteroaryl, where any two or more of R^{21}, R^{22}, R^{23},and R^{24} can be taken together with intervening atoms to form one or more optionally substituted 3- to 12-membered rings, optionally containing one or more heteroatoms.

116. The polycarbonate polyol composition of claim 115, wherein -E- is selected from the group consisting of:



; and mixtures of any two or more of these.

117. The polycarbonate polyol composition of claim 115, wherein -E- comprises predominantly $-CH_2CH_2-$ units derived from ethylene oxide.

118. The polycarbonate polyol composition of claim 115, wherein -E- comprises units derived from ethylene oxide in combination with amounts of more complex -E- groups derived from other epoxides.

119. The polycarbonate polyol composition of claim 115, wherein -E- comprises $-CH_2CH(CH_3)-$ groups derived from propylene oxide.

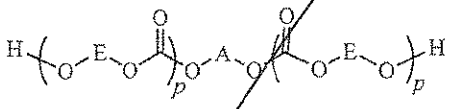
120. The polycarbonate polyol composition of claim 115, wherein -E- includes units derived from propylene oxide in combination -E- groups derived ethylene oxide.

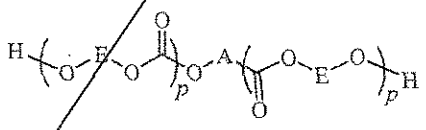
121. The polycarbonate polyol composition of claim 115, wherein -E- comprises units derived from propylene oxide in combination with lesser amounts of more complex -E- groups derived from other epoxides.

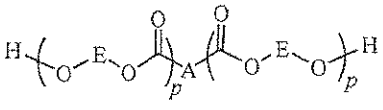
122. The polycarbonate polyol composition of claim 115, wherein -E- comprises units derived from propylene oxide in combination with units derived from a glycidyl ester.

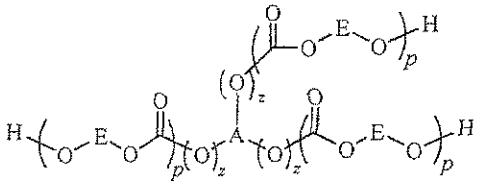
123. The polycarbonate polyol composition of claim 115, wherein -E- comprises units derived from propylene oxide in combination with units derived from a glycidyl ether.

124. The polycarbonate polyol composition of claim 115, wherein -E- comprises units derived from propylene oxide in combination with units derived from an epoxide of a C_{6-30} alpha olefin.

125. The polycarbonate polyol composition of claim 107, where chains of type P^1 have the formula: .

126. The polycarbonate polyol composition of claim 107, where chains of type P^1 have the formula: .

127. The polycarbonate polyol composition of claim 107, where chains of type P^1 have the formula: .

128. The polycarbonate polyol composition of claim 107, wherein chains of type P^1 have the formula: , where each z is independently 0 or 1.

129. The polycarbonate polyol composition of claim 107 wherein –A- comprises a polymer chain or oligomer selected from the group consisting of polyolefins, polyethers, polyesters, polycarbonates, polycarbonate polyethers and polyoxymethylene.

130. The polycarbonate polyol composition of claim 107 wherein –A- comprises a scaffold derived from a compound selected from the group consisting of: sugar alcohols, carbohydrates, saccharides, polysaccharides, starch, starch derivatives, lignins, lignans, partially hydrolyzed triglycerides, and derivatives of any of these materials.

131. A polyurethane composition formed by reaction of one or more isocyanates with one or more aliphatic polycarbonate polyols of any of claims 95-112.

132. An article of manufacture comprising the polycarbonate polyol composition of any one of claims 95-112.

133. An article of manufacture comprising the polyurethane composition of claim 131.

CLAIMS

What is claimed is:

1. An aliphatic polycarbonate polyol composition comprising an epoxide-CO_2 copolymer characterized in that the copolymer has:
an Mn between 400 and 20,000,
greater than 90% carbonate linkages,
and at least 98% of the end groups are hydroxyl groups.

2. The polycarbonate polyol composition of claim 1, comprising greater than 92% carbonate linkages.

3. The polycarbonate polyol composition of claim 1, comprising greater than 95% carbonate linkages.

4. The polycarbonate polyol composition of claim 1, comprising greater than 97% carbonate linkages.

5. The polycarbonate polyol composition of claim 1, comprising greater than 99% carbonate linkages.

6. The polycarbonate polyol composition of claim 1, having an Mn between 500 and 5,000 g/mol.

7. The polycarbonate polyol composition of claim 1, having an Mn between 800 and 4,000 g/mol.

8. The polycarbonate polyol composition of claim 1, having an Mn between 1,000 and 3,000 g/mol.

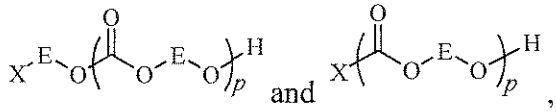
9. The polycarbonate polyol composition of claim 1, having an Mn of 1,000 g/mol.

10. The polycarbonate polyol composition of claim 1, having an Mn of 2,000 g/mol.

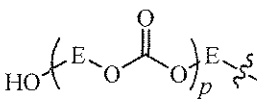
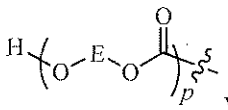
11. The polycarbonate polyol composition of claim 1, having an Mn of 4,000 g/mol.

12. The polycarbonate polyol composition of claim 1, having an Mn of 8,000 g/mol.

13. The polycarbonate polyol composition of claim 1, comprising polymer chains denoted P^1 and P^2, P^1 having the formula T-Y-A-(Y-T)$_n$ derived from a chain transfer agent having the formula Y-A-(Y)$_n$, with Y as defined below, and P^2 having a formula selected from the group consisting of:

 and ,

each -T is a polycarbonate chain having a formula independently selected from the group consisting of:

 and  wherein:

E is an optionally substituted C_2 unit derived from an epoxide, where E may represent a monomer unit derived from one type of epoxide, or a mixture of two or more types of epoxide, and

p ranges from 5 to 10,000;

each –Y group is independently a functional group capable of initiating chain growth of epoxide CO_2 copolymers selected from the group consisting of -OH, -C(O)OH, -C(OR^y)OH, -OC(R^y)OH, -NHR^y, -NHC(O)R^y, -NHC=NR^y; -NR^{y}C=NH; -NR^{y}C(NR$^y_2$)=NH; -NHC(NR$^y_2$)=NR^y; -NHC(O)OR^y, -NHC(O)NR$^y_2$; -C(O)NHR^y, -C(S)NHR^y, -OC(O)NHR^y, -OC(S)NHR^y, -SH, -C(O)SH, -B(OR^y)OH, -P(O)$_a$(R^y)$_b$(OR^y)$_c$(O)$_d$H, -OP(O)$_a$(R^y)$_b$(OR^y)$_c$(O)$_d$H, –N(R^y)OH, -ON(R^y)H; =NOH, =NN(R^y)H, where each occurrence of R^y is independently –H, or an optionally substituted

radical selected from the group consisting of C_{1-20} aliphatic, C_{1-20} heteroaliphatic, 3- to 12-membered heterocyclic, and 6- to 12-membered aryl, *a* and *b* are each independently 0 or 1, *c* is 0, 1 or 2, *d* is 0 or 1, and the sum of *a*, *b*, and *c* is 1 or 2 and where an acidic hydrogen atom bound in any of the above functional groups may be replaced by a metal atom or an organic cation and each Y group may be the same or different,

-A- is a covalent bond or a multivalent moiety;

X is a bound form of an anion capable of initiating only one polymer chain, comprising a halogen atom, an azide, an ester group, an ether group, or a sulfonic ester group;

and

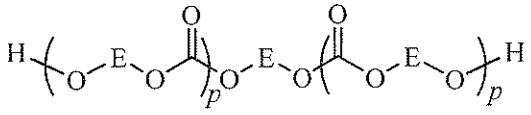
n is an integer between 1 and 10 inclusive;

wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 20:1.

14. The polycarbonate polyol composition of claim 13, wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 40:1.

15. The polycarbonate polyol composition of claim 13, wherein the ratio of P^1 polymer chains to P^2 polymer chains is greater than 100:1.

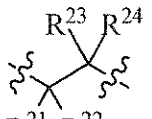
16. The polycarbonate polyol composition of any one of claims 13-15, further comprising polymer chains denoted P^{1a} having a formula:



17. The polycarbonate polyol composition of claim 16, wherein the ratio of P^1 polymer

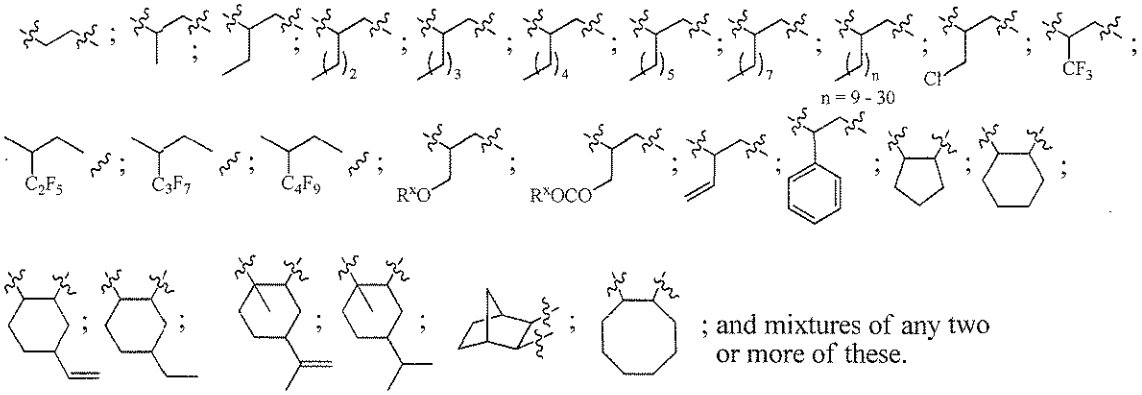
chains to P^{1a} polymer chains is greater than 20:1.

18. The polycarbonate polyol composition of any one of claims 13-15, wherein each E is



, where, R^{21}, R^{22}, R^{23}, and R^{24}, are each independently selected from the group consisting of: –H; and an optionally substituted group selected from C_{1-30} aliphatic; C_{6-14} aryl; 3- to 12-membered heterocycle, and 5- to 12-membered heteroaryl, where any two or more of R^{21}, R^{22}, R^{23},and R^{24} can be taken together with intervening atoms to form one or more optionally substituted 3- to 12-membered rings, optionally containing one or more heteroatoms.

19. The polycarbonate polyol composition of claim 18, wherein -E- is selected from the group consisting of:



; and mixtures of any two or more of these.

20. The polycarbonate polyol composition of claim 18, wherein -E- comprises predominantly $-CH_2CH_2-$ units derived from ethylene oxide, or wherein -E- comprises predominantly $-CH_2CH(CH_3)-$ groups derived from propylene oxide.

21. The polycarbonate polyol composition of claim 18, wherein -E- comprises units derived from ethylene oxide in combination with amounts of more complex -E- groups derived from other epoxides.

22. The polycarbonate polyol composition of claim 18, wherein -E- comprises -

$CH_2CH(CH_3)$- groups derived from propylene oxide.

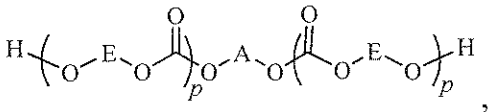
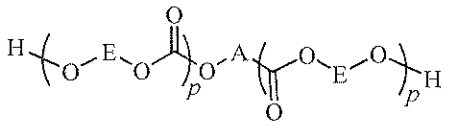
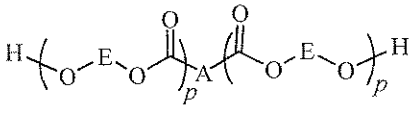
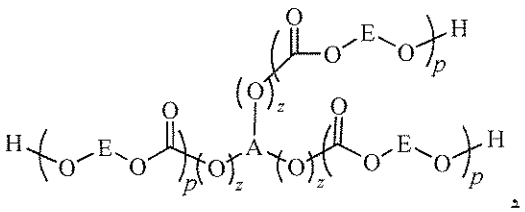
23. The polycarbonate polyol composition of claim 18, wherein -E- includes units derived from propylene oxide in combination -E- groups derived ethylene oxide.

24. The polycarbonate polyol composition of claim 18, wherein -E- comprises units derived from propylene oxide in combination with lesser amounts of more complex -E- groups derived from other epoxides.

25. The polycarbonate polyol composition of claim 18, wherein -E- comprises units derived from propylene oxide in combination with units derived from a glycidyl ester.

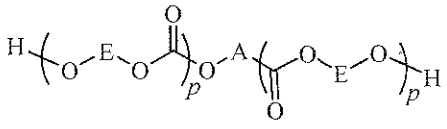
26. The polycarbonate polyol composition of claim 18, wherein -E- comprises units derived from propylene oxide in combination with units derived from a glycidyl ether.

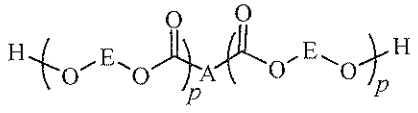
27. The polycarbonate polyol composition of claim 18, wherein -E- comprises units derived from propylene oxide in combination with units derived from an epoxide of a $C_{6\text{-}30}$ alpha olefin.

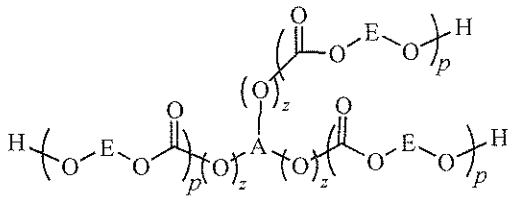
28. The polycarbonate polyol composition of claim 13, where chains of type P^1 have the formula:  ,  ,  , or  ,

wherein each *z* is independently 0 or 1.

29. The polycarbonate polyol composition of claim 13, where chains of type P^1 have the

formula:  .

30. The polycarbonate polyol composition of claim 13, where chains of type P^1 have the formula:  .

31. The polycarbonate polyol composition of claim 13, wherein chains of type P^1 have the formula:  , where each *z* is independently 0 or 1.

32. The polycarbonate polyol composition of claim 13, wherein –A- comprises a polymer chain or oligomer selected from the group consisting of polyolefins, polyethers, polyesters, polycarbonates, polycarbonate polyethers and polyoxymethylene.

33. The polycarbonate polyol composition of claim 13, wherein –A- comprises a scaffold derived from a compound selected from the group consisting of: sugar alcohols, carbohydrates, saccharides, polysaccharides, starch, starch derivatives, lignins, lignans, partially hydrolyzed triglycerides, and derivatives of any of these materials.

34. The polycarbonate polyol composition of claim 1 or 13, wherein at least 99% of the end groups of the polycarbonate polyol are OH groups.

35. The polycarbonate polyol composition of claim 1 or 13, wherein the PDI of the polycarbonate polyol is less than 1.6.

36. The polycarbonate polyol composition of claim 1 or 13, wherein the PDI of the

polycarbonate polyol is less than 1.2.

37. The polycarbonate polyol composition of claim 1 or 13, wherein the Y-A-$(Y)_n$ moiety is derived from a chain transfer agent selected from a polyhydric alcohol, a polycarboxylic acid, or a hydroxy acid.

38. The polycarbonate polyol composition of claim 1 or 13, wherein the Y-A-$(Y)_n$ moiety is derived from a chain transfer agent, wherein at least one Y group is a carboxylic acid and one or more additional Y groups are –OH.

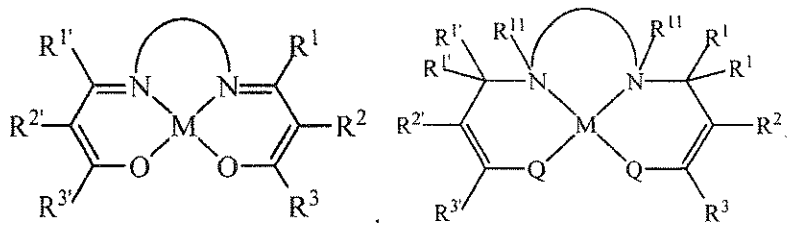
39. A polyurethane composition formed by reaction of one or more isocyanates with an aliphatic polycarbonate polyol of any one of claims 1-15.

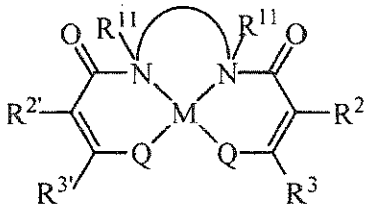
40. An article of manufacture comprising an aliphatic polycarbonate polyol composition of any one of claims 1-15.

41. An article of manufacture comprising the polyurethane composition of claim 39.

42. The polyurethane composition of claim 39, wherein the composition comprises a foam or coating.

43. A polymerization formulation for the synthesis of aliphatic polycarbonate polyols having a high percentage of –OH end groups, the formulation comprising:
a metal complex having the formula L_p-M-$(L_I)_m$, where L_p is a permanent ligand set, M is a metal atom, and L_I is a ligand that is a polymerization initiator, and m is an integer between 0 and 2 inclusive representing the number of initiating ligands present;
wherein Lp-M has a formula selected from the group consisting of:


; and


;

wherein Q, at each occurrence is independently O or S;

R^1 and $R^{1'}$ are independently selected from the group consisting of: –H, optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; and R^{21};

R^2 and $R^{2'}$ are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; R^{14}; R^{20}; and R^{21};

R^3 and $R^{3'}$ are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle, and R^{21};

⌒ represents an optionally substituted moiety covalently linking two nitrogen atoms, where any of [$R^{2'}$ and $R^{3'}$], [R^2 and R^3], [R^1 and R^2], and [$R^{1'}$ and $R^{2'}$] may optionally be taken together with intervening atoms to form one or more rings which may in turn be substituted with one or more groups selected from R^{14}; R^{20}; and R^{21}; and where

R^{14} at each occurrence is independently selected from the group consisting of: halogen; optionally substituted C_1 to C_{12} aliphatic; optionally substituted 3- to 14-membered carbocycle; optionally substituted 3- to 14-membered heterocycle; $–OR^{10}$; $–OC(O)R^{13}$; $–OC(O)OR^{13}$; $–OC(O)NR^{11}R^{12}$; –CN; –CNO; $–C(R^{13})_zH_{(3-z)}$; $–C(O)R^{13}$; $–C(O)OR^{13}$; $–C(O)NR^{11}R^{12}$; $–NR^{11}R^{12}$; $–NR^{11}C(O)R^{13}$; $–NR^{11}C(O)OR^{13}$; $–NR^{11}SO_2R^{13}$; $–N^+R^{11}R^{12}R^{13}$ X^-; $–P^+(R^{11})_3$ X^-; $–P(R^{11})_3{=}N^+{=}P(R^{11})_3$ X^-; $–As^+R^{11}R^{12}R^{13}$ X^-; –NCO; $–N_3$; $–NO_2$; $–S(O)_xR^{13}$; and $–SO_2NR^{11}R^{12}$,

R^{20} at each occurrence is independently selected from the group consisting of: halogen; $-OR^{10}$; $-OC(O)R^{13}$; $-OC(O)OR^{13}$; $-N^{+}(R^{11})_3$ X^{-}; $-P^{+}(R^{11})_3$ X^{-}; $-P(R^{11})_3{=}N^{+}{=}P(R^{11})_3$ X^{-}; $-As^{+}R^{11}R^{12}R^{13}$ X^{-}; $-OC(O)NR^{11}R^{12}$; $-CN$; $-CNO$; $-C(O)R^{13}$; $-C(O)OR^{13}$; $-C(O)NR^{11}R^{12}$; $-C(R^{13})_zH_{(3-z)}$; $-NR^{11}R^{12}$; $-NR^{11}C(O)R^{13}$; $-NR^{11}C(O)OR^{13}$; $-NCO$; $-NR^{11}SO_2R^{13}$; $-S(O)_xR^{13}$; $-S(O)_2NR^{11}R^{12}$; $-NO_2$; $-N_3$; and $-Si(R^{13})_{(3-z)}[(CH_2)_kR^{14}]_z$,

R^{21} at each occurrence is independently selected from the group consisting of: $-(CH_2)_kR^{20}$; $-(CH_2)_k$-Z"-$(CH_2)_kR^{20}$; $-C(R^{17})_zH_{(3-z)}$; $-(CH_2)_kC(R^{17})_zH_{(3-z)}$; $-(CH_2)_m$-Z"-$(CH_2)_mC(R^{17})_zH_{(3-z)}$; $-(CH_2)_k$-Z"-R^{16};

X^{-} is any anion,

Z" is a divalent linker selected from the group consisting of $-(CH{=}CH)_a-$; $-(CH{\equiv}CH)_a-$; -C(O)-; $-C(=NOR^{11})-$; $-C(=NNR^{11}R^{12})-$; -O-; -OC(O)-; -C(O)O-; -OC(O)O-; $-N(R^{11})-$; $-N(C(O)R^{13})-$; $-C(O)NR^{13}-$; $-N(C(O)R^{13})O-$; $-NR^{13}C(O)R^{13}N-$; $-S(O)_x-$; a polyether; and a polyamine,

R^{10} at each occurrence is independently selected from the group consisting of: –H; optionally substituted C_{1-12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14-membered heterocycle $-S(O)_2R^{13}$; $-Si(R^{15})_3$; $-C(O)R^{13}$; and a hydroxyl protecting group,

R^{11} and R^{12} at each occurrence are independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; an optionally substituted 3- to 14-membered heterocycle; where two or more R^{11} or R^{12} groups can optionally be taken together with intervening atoms to form an optionally substituted 3- to 10-membered ring,

R^{13} at each occurrence is independently selected from the group consisting of: –H; optionally substituted C_1 to C_{12} aliphatic; an optionally substituted 3- to 14-membered carbocycle; and optionally substituted 3- to 14-membered heterocycle, where two or more R^{13} groups on the same molecule may optionally be taken together to form ring.

R^{15} at each occurrence is independently selected from the group consisting of: optionally substituted C_{1-12} aliphatic, an optionally substituted 3- to 14-membered carbocycle; and an optionally substituted 3- to 14-membered heterocycle,

a is 1, 2, 3, or 4,

k is independently at each occurrence an integer from 1 to 8, inclusive,

m is 0 or an integer from 1 to 8, inclusive,

x is 0, 1, or 2, and

z is 1, 2, or 3;

and

a chain transfer agent having a plurality of sites capable of initiating copolymerization of epoxides and CO_2; wherein the chain transfer agent and metal complex are present in a molar ratio ranging from 50:1 to 500:1, 500:1 to 1000:1, or greater than 1000:1;

wherein the chain transfer agent has a structure $Y\text{-}A\text{-}(Y)_n$,

where:

each –Y group is independently a functional group capable of initiating chain growth of epoxide CO_2 copolymers and each Y group may be the same or different;

-A- is a covalent bond or a multivalent moiety; and

n is an integer between 1 and 10, inclusive;

wherein said aliphatic polycarbonate polyols have an average molecular weight number between 400 g/mol and 20,000 g/mol, and at least 98% of the end groups are hydroxyl groups.

44. The polymerization formulation of claim 43, wherein the metallosalenate metal complex is a cobalt salen complex.

45. A method for the synthesis of aliphatic polycarbonate polyols having a high percentage of –OH end groups, the method comprising the steps of:

a) contacting a reaction mixture comprising one or more epoxides with a polymerization formulation of claim 43 in the presence of carbon dioxide, wherein the molar ratio of metal complex to epoxide ranges from 1:100 to 1:1,000,000;

b) allowing the polymerization reaction to proceed until a desired molecular weight aliphatic polycarbonate polyol has formed, wherein in the aliphatic polycarbonate polyol composition, at least 98% of the end groups are hydroxyl groups, and wherein the polycarbonate polyol has an average molecular weight number between 400 and 20,000;

and

c) terminating the polymerization.

46. The method of claim 45, wherein at least 99% of the end groups of the polycarbonate polyol formed are OH groups.

47. The method of claim 45, wherein at least 50% of epoxide in the reaction mixture is converted to aliphatic polycarbonate polyol.

48. The method of claim 45, wherein the molar ratio of chain transfer agent to metal complex is greater than 1000:1.

49. The method of claim 45, wherein the PDI of the polycarbonate polyol formed is less than 1.6.

50. The method of claim 45, wherein the PDI of the polycarbonate polyol formed is less than 1.2.

51. The method of claim 45, wherein more than 80% of the linkages formed by the metal complex are carbonate linkages.

52. The method of claim 45, wherein more than 90% of the linkages formed by the metal complex are carbonate linkages.

53. The method of claim 45, wherein more than 95% of the linkages formed by the metal complex are carbonate linkages.

54. The method of claim 45, wherein the epoxide comprises propylene oxide.

55. The method of claim 54, wherein the head-to-tail ratio of the polycarbonate polyol is

greater than 80%.

56. The method of claim 54, wherein the head-to-tail ratio of the polycarbonate polyol is greater than 90%.

57. The method of claim 54, wherein the head-to-tail ratio of the polycarbonate polyol is greater than 95%.

58. The method of claim 45, wherein less than 5% cyclic carbonate is formed.

59. The method of claim 45, wherein the reaction mixture further comprises a chain transfer agent ~~is~~ selected from the group consisting of: water; polyhydric alcohols; polyacids; hydroxy acids; primary amines; polyamines, amino alcohols, amino acids, aldehyde hydrates, ketone hydrates, formaldehyde, polyhydric thiols, hydroxy thiols, amino thiols, and mercapto acids, boronic acids, and mixtures of any two or more of these.

60. The method of claim 45, wherein the reaction mixture further comprises a chain transfer agent ~~is~~ selected from the group consisting of: water; polyhydric alcohols; polyacids; and hydroxy acids, and mixtures of any two or more of these.

61. The method of claim 45, wherein less than 1% cyclic carbonate is formed.