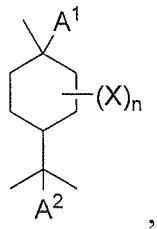
WHAT IS CLAIMED:

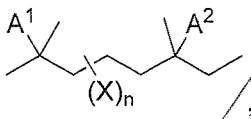
1. A method for producing a telechelic polyolefin, comprising contacting a terpene initiator with a Lewis acid in the presence of one or more monomers, wherein the terpene initiator contains

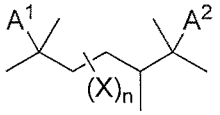
(a) one or more tertiary carbons containing a leaving group, and

(b) one or more functional groups, wherein the one or more functional groups are bonded to a primary or secondary carbon and are unmodified under polymerization conditions.

2. The method of claim 1, wherein the terpene initiator is selected from:



,


, and


wherein:

A^1 and A^2 are each, individually at each occurrence, a leaving group or –H, wherein at least one of A^1 and A^2 is a leaving group;

X is -OH, -F, -Cl, -Br, -I, =O, $-OC(O)R^A$, $-OR^A$, -NC, -NCO, -OCN, -SH, $-SR^A$,

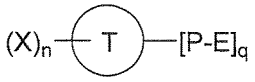
$-S(O)R^A$, $-S(O)_2R^A$, -SCN, $-NO_2$, or $-OS(O)_2R^A$,

wherein R^A is alkyl, alkenyl, or alkynyl, and

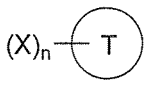
X is bonded to a primary or secondary carbon; and

n is an integer from 1-3.

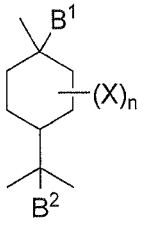
3. The method of claim 1, wherein the method forms a telechelic polyolefin of the following formula:

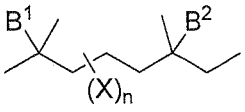


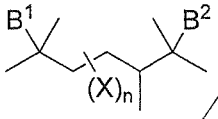
wherein:



is selected from



,


, and


wherein:

B^1 and B^2, independently at each occurrence, are H or a bond to P,

wherein at least one of B^1 and B^2 is a bond to P;

X is -OH, -F, -Cl, -Br, -I, =O, $-OC(O)R^A$, $-OR^A$, -NC, -NCO, -OCN, -SH, $-SR^A$, $-S(O)R^A$, $-S(O)_2R^A$, -SCN, $-NO_2$, or $-OS(O)_2R^A$,

wherein R^A is alkyl, alkenyl, or alkynyl, and

X is bonded to a primary or secondary carbon;

n is an integer from 1-3;

P is a divalent polyolefin group

E is an end-cap group; and

q is an integer from 1-2.

4. The method of claim 2, wherein X is –OH, $-OR^A$, $-OC(O)R^A$, -F, -Cl, or –Br, wherein R^A is, independently at each occurrence, alkyl of 1-3 carbons.

5. The method of claim 2, wherein X is –OH.

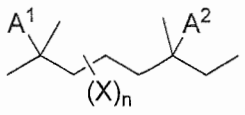
6. The method of claim 2, wherein the leaving group is, independently at each occurrence, -Cl, -Br, –I, or $-OC(O)R^N$, wherein R^N is alkyl having 1 to 6 carbons.

7. The method of claim 2, wherein n is 1.

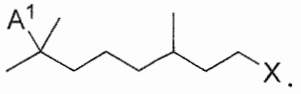
8. The method of claim 2, wherein one of A^1 or A^2 is H.

9. The method of claim 2, wherein X is bonded to a primary carbon.

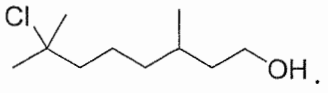
10. The method of claim 2, wherein the terpene initiator is:



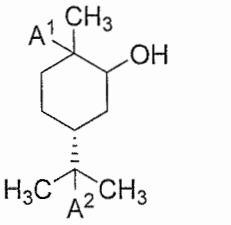
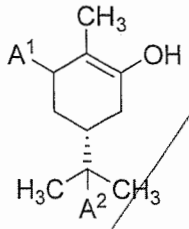
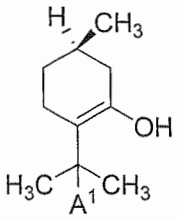
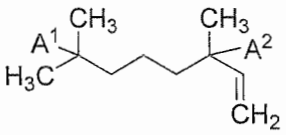
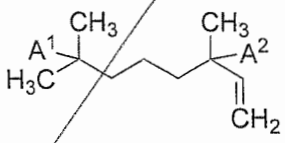
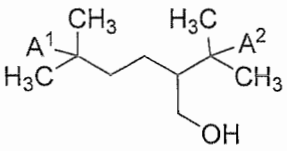
11. The method of claim 10, wherein the terpene initiator is



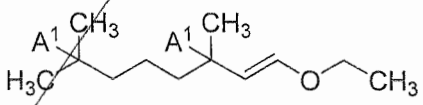
12. The method of claim 10, the terpene initiator is



13. The method of claim 1, wherein the terpene initiator is

or



wherein A^1 and A^2 are each, independently, -Br, -Cl, or -I.

14. The method of claim 1, wherein the terpene initiator contains 10 carbon atoms, excluding any carbon atoms that are a part of the one or more leaving groups or one or more functional groups.

15. The method of claim 1, further comprising adding one or more quenching agents.

16. The method of claim 15, wherein the quenching agent is

(a) allyltrimethylsilane;

(b) methallyltrimethylsilane;

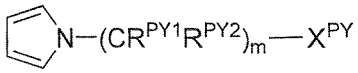
(c) 1,1 diphenylethylene;

(d) furan or substituted furan;

(e) thiophene or substituted thiophene;

(f) triphenylamine;

(g) a compound having the following formula:



wherein R^{PY1} and R^{PY2} are independently in each $-(CR^{PY1}R^{PY2})-$ unit selected from the group consisting of hydrogen and alkyl of 1 to 6 carbon atoms;

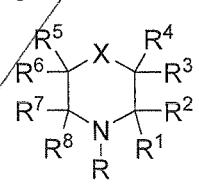
m is an integer from 1 to 20; and

X is selected from the group consisting of hydrogen, alkyl, aryl, alkaryl, alkoxy, heteroaryl, nitro, ureido, $-OC(O)R^{PY3}$, $-C(O)R^{PY4}$, $-C(O)OR^{PY5}$,

$-C(O)NR^{PY6}R^{PY7}$, $-P(R^{PY8})_3$, $-P(OR^{PY9})_3$, $-SR^{PY10}$, $-OSO_3R^{PY11}$, and $-S(O)R^{PY12}$;

wherein R^{PY3} is alkyl or alkenyl; and R^{PY4}, R^{PY5}, R^{PY7}, R^{PY8}, R^{PY9}, R^{PY10}, R^{PY11}, and R^{PY12} are alkyl;

(h) a compound having the following formula:



wherein:

R^1 through R^8 are independently hydrogen, alkyl from 1 to 20 carbon atoms, aryl from 6 to about 20 carbon atoms, alkaryl from about 7 to 30 carbon atoms, or aralkyl from about 7 to 30 carbon atoms;

R is hydrogen, alkyl from 1 to 20 carbon atoms, aryl from 6 to about 20 carbon atoms, alkaryl from about 7 to 30 carbon atoms, or aralkyl from about 7 to 30 carbon atoms; and

X is oxygen or sulfur;

with the proviso that when R is hydrogen or methyl then R^1, R^2, R^7 and R^8 must be other than hydrogen unless one of R^1 or R^2 and one of R^7 or R^8 is independently branched alkyl of about 3 to 20 carbon atoms, aryl, alkaryl or aralkyl;

(i) a compound having the following formula:

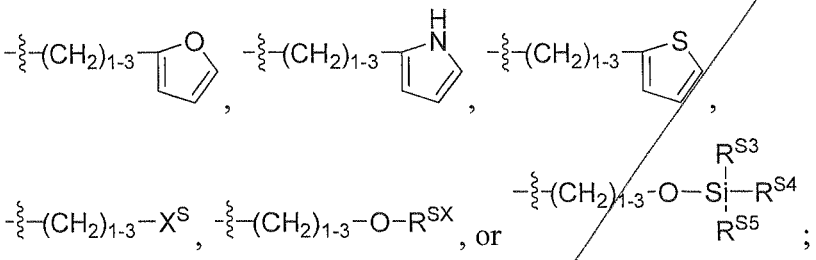
$$R^1\text{-}S\text{-}R^2$$

wherein R^1 and R^2, are each, independently, hydrocarbyl;

(j) a compound having the following formula:

$$R^{SA}\,S\text{-}S\text{-}R^{SB}$$

wherein R^{SA} and R^{SB} are each, independently, alkyl, aryl, aralkyl, alkaryl,



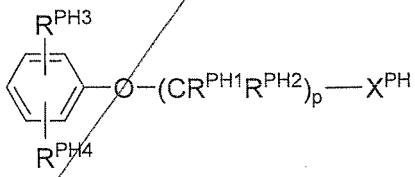
wherein X^S is halo or a pseudohalide;

R^{SX} is alkyl or aryl;

R^{S3} is tert-butyl; and

R^{S4} and R^{S5} are each, independently, alkyl, aryl, aralkyl, or alkaryl; or

(k) a compound having the following formula:

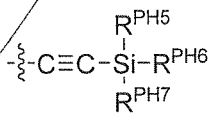


B

wherein R^{PH1} and R^{PH2} are each, independently in each $-(CR^{PH1}R^{PH2})$ unit, H or alkyl, and p is an integer from 0-20, wherein

(1) if p is 0, then R^{PH3} and R^{PH4} are each, independently, alkyl, and X^{PH} is H;

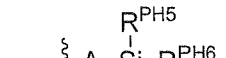
(2) if p is 1, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and X^{PH} is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, or



wherein R^{PH5}-R^{PH7} are each, independently, alkyl or aryl;

(3) if p is 2, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and X^{PH} is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, $-OC(O)R^{PH8}$, -

$C(O)OR^{PH9}$,

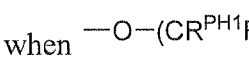
$-C(O)NR^{PH10}R^{PH11}$, or ; 

wherein A is or a single bond,

R^{PH5} to R^{PH7} are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, $NR^{PH10}R^{PH11}$, -F, -Cl, -Br, -I, or -At,

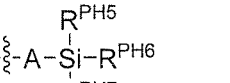
R^{PH8} is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

R^{PH9} to R^{PH11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, or

when  is ortho to R^{PH4}, then X^{PH} and R^{PH4}, together, with the atoms to which X^{PH} and R^{PH4} are attached, may form a ring; and

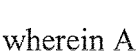
(4) if p is 3-20, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, aryloxy, heteroaryloxy, alkaryloxy, -OH, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$,



, or

$-NR^{PHX}R^{PHY}$;

wherein A is  or a single bond,

R^{PHX} and R^{PHY} are each, independently, H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, or $-C(O)R^{PHZ}$,

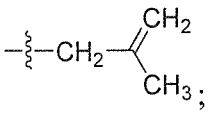
wherein R^{PHZ} is H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, $-OR^{PH8}$, or $-NR^{PH10}R^{PH11}$;

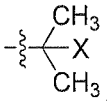
R^{PH5} to R^{PH7} are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, $NR^{PH10}R^{PH11}$, -F, -Cl, -Br, -I, or -At,

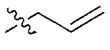
R^{PH8} is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and R^{PH9} to R^{PH11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl; or

(l) butadiene.

17. The method of claim 3, wherein the end-cap group is:

(a) ;

(b) , wherein X is a halide;

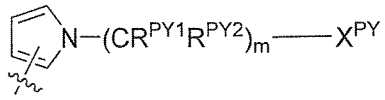
(c) ;

(d) a 1-substituted-1,1-diaryl ethylene group;

(e) furan or substituted furan;

(f) thiophene or substituted thiophene;

(g) triphenylamine;

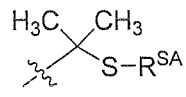
(h) ,

wherein R^{PY1} and R^{PY2} are independently in each $-(CR^{PY1}R^{PY2})-$ unit selected from the group consisting of hydrogen and alkyl from 1 to 6 carbon atoms;

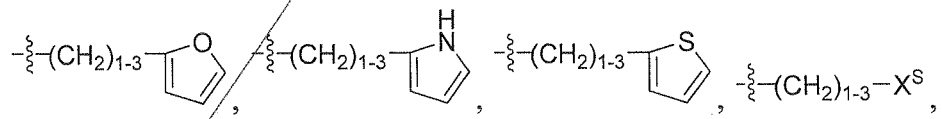
m is an integer from 1 to 20; and

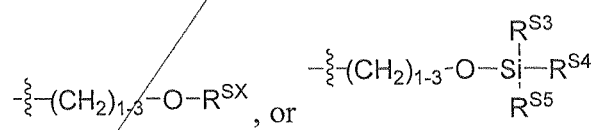
X^{PY} is selected from the group consisting of hydrogen, alkyl, aryl, alkaryl, alkoxy, heteroaryl, nitro, ureido, $-OC(O)R^{PY3}$, $-C(O)R^{PY4}$, $-C(O)OR^{PY5}$, $-C(O)NR^{PY6}R^{PY7}$, $-P(R^{PY8})_3$, $-P(OR^{PY9})_3$, $-SR^{PY10}$, $-OSO_3R^{PY11}$, and $-S(O)R^{PY12}$;

wherein R^{PY3} is alkyl or alkenyl; and R^{PY4}, R^{PY5}, R^{PY7}, R^{PY8}, R^{PY9}, R^{PY10}, R^{PY11}, and R^{PY12} are alkyl;

(i) ,

wherein R^{SA} is alkyl, aryl, aralkyl, alkaryl,

,

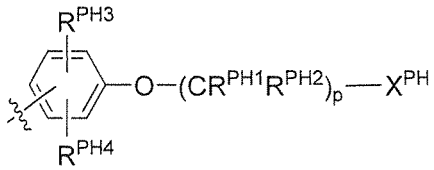
, or ;

X^S is halo or a pseudohalide;

R^{SX} is alkyl or aryl;

R^{S3} is tert-butyl; and

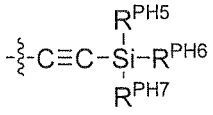
R^{S4} and R^{S5} are each, independently, alkyl, aryl, aralkyl, or alkaryl; or

(j)  , wherein

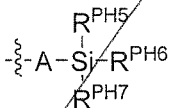
R^{PH1} and R^{PH2} are each, independently in each $-(CR^{PH1}R^{PH2})$ unit, H or alkyl, and p is an integer from 0-20, wherein

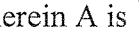
(1) if p is 0, then R^{PH3} and R^{PH4} are each, independently, alkyl, and X^{PH} is H;

(2) if p is 1, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and X^{PH} is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, or

 ,

wherein R^{PH5}-R^{PH7} are each, independently, alkyl or aryl;

(3) if p is 2, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and X^{PH} is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$, or  ;

wherein A is  or a single bond,

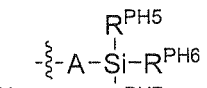
R^{PH5} to R^{PH7} are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, $NR^{PH10}R^{PH11}$, -F, -Cl, -Br, -I, or -At,

R^{PH8} is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

R^{PH9} to R^{PH11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, or when $-O-(CR^{PH1}R^{PH2})_p-X^{PH}$ is ortho to R^{PH4}, then X^{PH} and R^{PH4}, together, with the atoms to which X^{PH} and R^{PH4} are attached, may form a ring; and

(4) if p is 3-20, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, aryloxy, heteroaryloxy, alkaryloxy, -OH, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN,

-NCS, -SCN, -OC(O)R^{PH8}, -C(O)OR^{PH9}, –C(O)N$R^{PH10}R^{PH11}$, , or -N$R^{PHX}R^{PHY}$;

wherein A is or a single bond,

R^{PHX} and R^{PHY} are each, independently, H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, C(O)R^{PHZ},

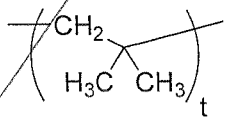
wherein R^{PHZ} is H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, -OR^{PH8}, or -N$R^{PH10}R^{PH11}$;

R^{PH5} to R^{PH7} are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, N$R^{PH10}R^{PH11}$, -F, -Cl, -Br, -I, or –At,

R^{PH8} is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and R^{PH9} to R^{PH11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl; or

(k) an allyl halide.

18. The method of claim 3, wherein P is



wherein t is an integer from 2-20,000.

19. The method of claim 1, wherein the one or more monomers is isobutene.

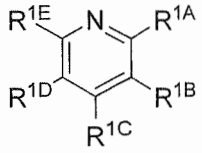
20. The method of claim 1, wherein the one or more monomers is styrene.

21. The method of claim 1, wherein the Lewis acid is a titanium halide, aluminum halide, boron halide, or an alkyl aluminum halide.

22. The method of claim 1, wherein the Lewis acid is $TiCl_4$.

23. The method of claim 1, wherein the method is performed in the presence of one or more electron donors.

24. The method of claim 23, wherein the one or more electron donors is



wherein R^{1A}, R^{1B}, R^{1C}, R^{1D}, and R^{1E} are each, independently, hydrogen or hydrocarbyl; or R^{1A} and R^{1B}, or R^{1B} and R^{1C}, or R^{1C} and R^{1D}, or R^{1D} and R^{1E} independently form a fused aliphatic ring of about 3 to about 7 carbon atoms or a fused aromatic ring of about 5 to about 7 carbon atoms.

25. The method of claim 24, wherein the one or more electron donors is 2,6-dimethylpyridine, 2,6-di-tert-butylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, 2-methylpyridine, or pyridine.

26. The method of claim 1, wherein the method is performed in the presence of a common ion salt or common ion salt precursor.

27. The method of claim 26, wherein the common ion salt precursor is tetra-n-butylammonium chloride, tetra-n-butylammonium bromide, or tetra-n-butylammonium iodide.

28. The method of claim 1, wherein greater than 90% of the monomer is consumed prior to adding the quenching agent.

29. The method of claim 1, wherein one or more aliquots of additional monomer are added to the polymerization after the initial monomer charge, wherein each individual aliquot of additional monomer is consumed or partially consumed prior to adding a subsequent aliquot of additional monomer or adding the quenching agent.

30. The method of claim 1, wherein the Lewis acid is deactivated with one or more terminators.

31. The method of claim 15, wherein the Lewis acid is deactivated with one or more terminators after adding the one or more quenching agents.

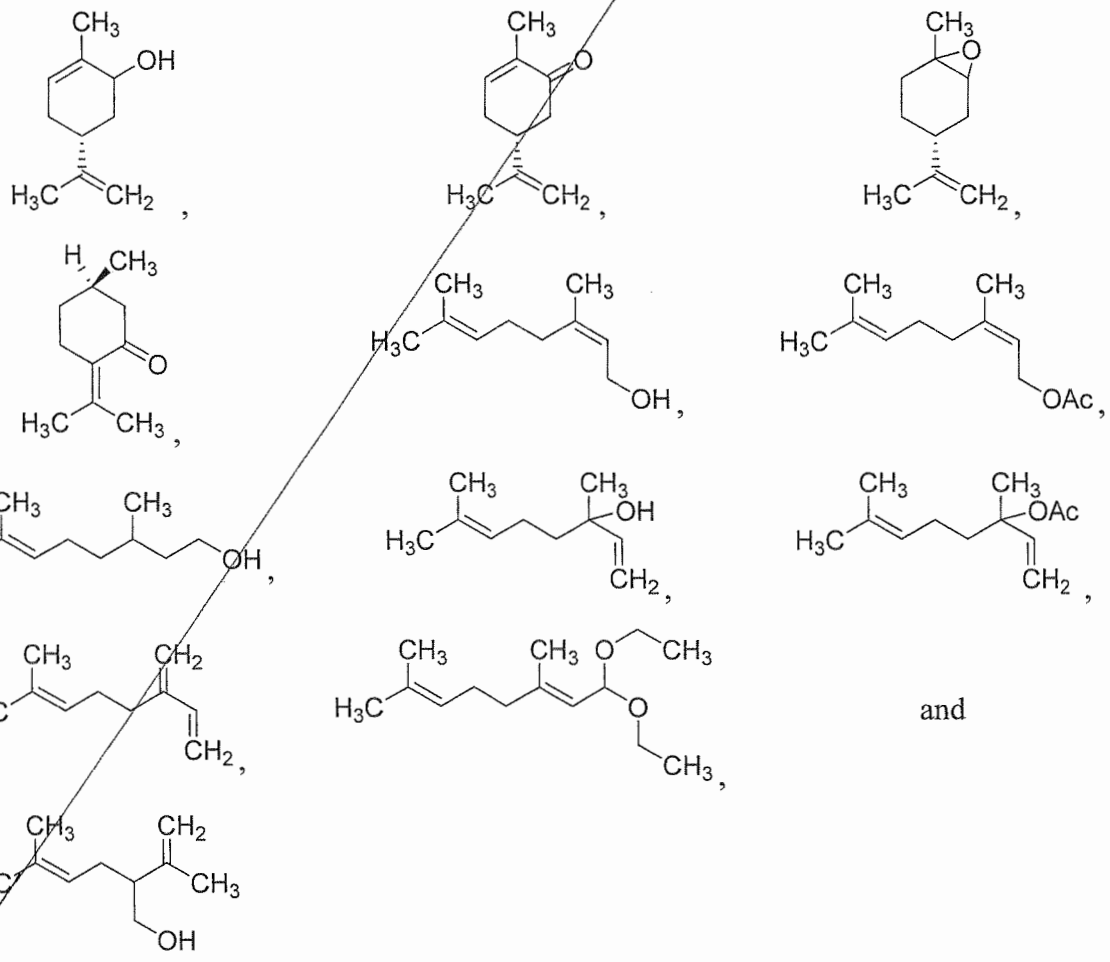
32. The method of claim 3, wherein the Lewis acid is deactivated with one or more terminators and E is a tert-halide.

33. The method of claim 1, wherein the telechelic polyolefin has a polydispersity index of less than 1.9.

34. The method of claim 1, wherein the monomer is polymerized under quasiliving polymerization conditions.

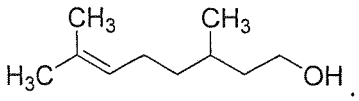
35. The method of claim 1, wherein the terpene initiator is derived by hydrohalogenation of a unsaturated terpene.

36. The method of claim 1, wherein the terpene initiator is derived from a compound selected from:

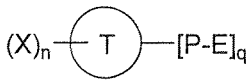


and

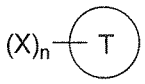
37. The method of claim 36, wherein the terpene initiator is derived from:

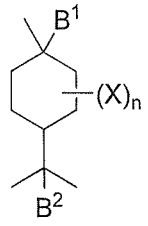
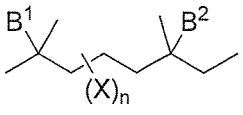
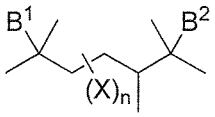


38. A compound having the following formula:



wherein:

 is selected from

, , and 

wherein:

B^1 and B^2, independently at each occurrence, are H or a bond to P,

wherein at least one of B^1 and B^2 is a bond to P;

X is -OH, -F, -Cl, -Br, -I, -NC, -NCO, -OCN, -SH, $-SR^A$, $-S(O)R^A$, $-S(O)_2R^A$, -SCN, $-OR^A$, $-NO_2$, $-OS(O)_2R^A$, =O, or $-OC(O)R^A$,

wherein R^A is alkyl, alkenyl, or alkynyl,

and X is bonded to a primary or secondary carbon;

n is an integer from 1-3;

P is a divalent polyolefin group

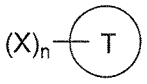
E is an end-cap group; and

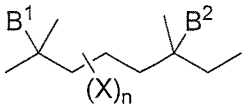
q is an integer from 1-2.

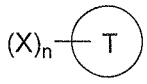
39. The compound of claim 38, wherein X is -OH, $-OR^A$, $-OC(O)R^A$, -F, -Cl, or -Br, wherein R^A is, independently at each occurrence, alkyl of 1-3 carbons.

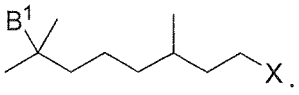
40. The compound of claim 38, wherein n is 1.

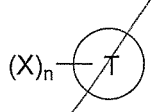
41. The compound of claim 38, wherein X is bonded to a primary or secondary carbon.

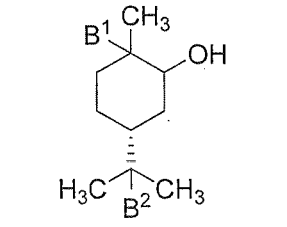
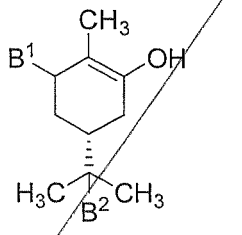
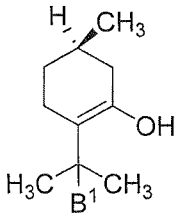
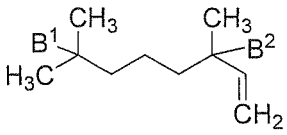
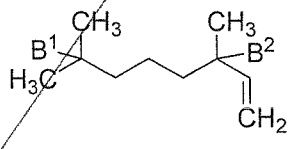
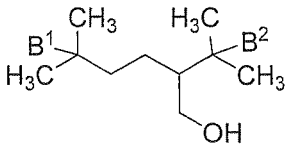
42. The compound of claim 38, wherein  is:



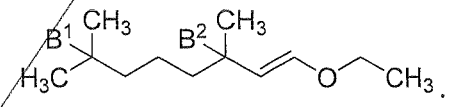
43. The compound of claim 38, wherein  is:



44. The compound of claim 38, wherein  is

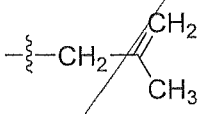







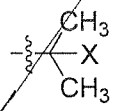
or

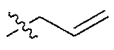


wherein B^1 and B^2 are each a bond to P.

45. The compound of claim 38, wherein the end-cap group is:

(a) ;

(b) , wherein X is a halide;

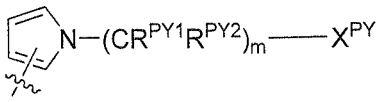
(c) ;

(d) a 1-substituted-1,1-diaryl ethylene group;

(e) furan or substituted furan;

(f) thiophene or substituted thiophene;

(g) triphenylamine;

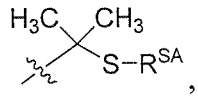
(h) ,

wherein R^{PY1} and R^{PY2} are independently in each -($CR^{PY1}R^{PY2}$)- unit selected from the group consisting of hydrogen and alkyl from 1 to 6 carbon atoms;

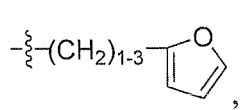
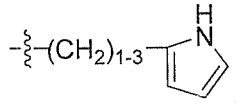
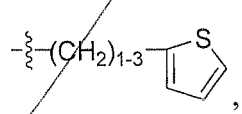
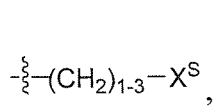
m is an integer from 1 to 20; and

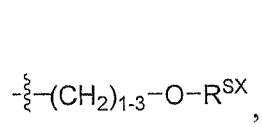
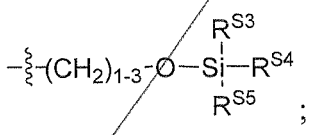
X^{PY} is selected from the group consisting of hydrogen, alkyl, aryl, alkaryl, alkoxy, heteroaryl, nitro, ureido, -$OC(O)R^{PY3}$, -$C(O)R^{PY4}$, -$C(O)OR^{PY5}$, -$C(O)NR^{PY6}R^{PY7}$, -$P(R^{PY8})_3$, -$P(OR^{PY9})_3$, -SR^{PY10}, -OSO_3R^{PY11}, and -$S(O)R^{PY12}$;

wherein R^{PY3} is alkyl or alkenyl; and R^{PY4}, R^{PY5}, R^{PY7}, R^{PY8}, R^{PY9}, R^{PY10}, R^{PY11}, and R^{PY12} are alkyl;

(i) ,

wherein R^{SA} is alkyl, aryl, aralkyl, alkaryl,

, , , ,

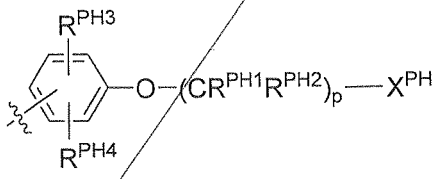
, or ;

X^S is halo or a pseudohalide;

R^{SX} is alkyl or aryl;

R^{S3} is tert-butyl; and

R^{S4} and R^{S5} are each, independently, alkyl, aryl, aralkyl, or alkaryl; or

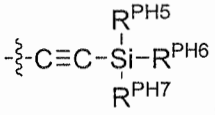
(j) , wherein

R^{PH1} and R^{PH2} are each, independently in each –($CR^{PH1}R^{PH2}$) unit, H or alkyl, and p is an integer from 0-20, wherein

(1) if p is 0, then R^{PH3} and R^{PH4} are each, independently, alkyl, and X^{PH} is H;

(2) if p is 1, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and

X^{PH} is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, or

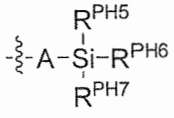


,

wherein R^{PH5}-R^{PH7} are each, independently, alkyl or aryl;

(3) if p is 2, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and

X^{PH} is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$,

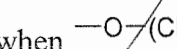


$-C(O)NR^{PH10}R^{PH11}$, or ;

wherein A is  or a single bond,

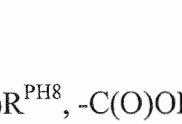
R^{PH5} to R^{PH7} are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, $NR^{PH10}R^{PH11}$, -F, -Cl, -Br, -I, or -At,

R^{PH8} is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

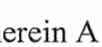
R^{PH9} to R^{PH11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, or when  is ortho to R^{PH4}, then X^{PH} and R^{PH4}, together with the atoms to which X^{PH} and R^{PH4} are attached, may form a ring; and

(4) if p is 3-20, then R^{PH3} and R^{PH4} are each, independently H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, aryloxy, heteroaryloxy, alkaryloxy, -OH, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN,



-NCS, -SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$, , or $-NR^{PHX}R^{PHY}$;

wherein A is  or a single bond,

R^{PHX} and R^{PHY} are each, independently, H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, $C(O)R^{PHZ}$,

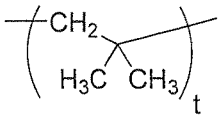
wherein R^{PHZ} is H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, $-OR^{PH8}$, or $-NR^{PH10}R^{PH11}$;

R^{PH5} to R^{PH7} are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, $NR^{PH10}R^{PH11}$, -F, -Cl, -Br, -I, or –At,

R^{PH8} is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and R^{PH9} to R^{PH11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl; or

(k) an allyl halide.

46. The compound of claim 38, wherein P is

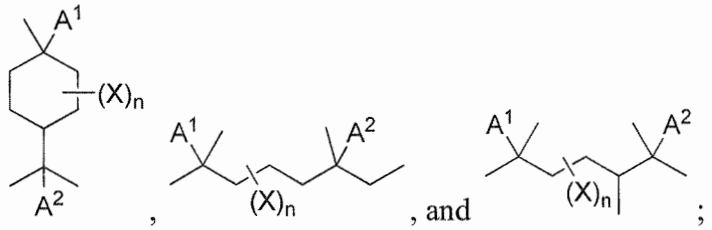


wherein t is an integer from 2-20000.

47. The compound of claim 38, wherein the compound has a polydispersity index of less than 1.9.

Claims

1. A method for producing a telechelic polyolefin, comprising contacting a terpene initiator with a Lewis acid in the presence of one or more monomers, wherein the terpene initiator is selected from:

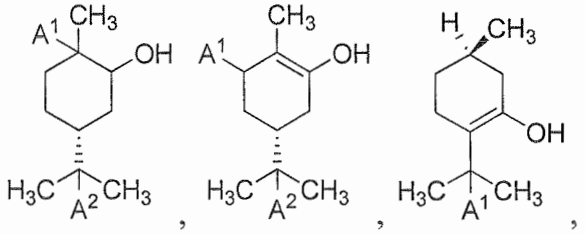
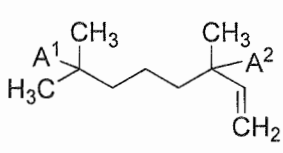
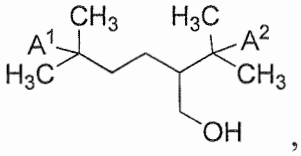
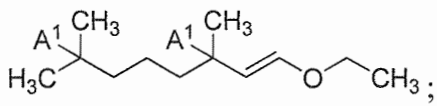
(a) , , and ;

wherein:

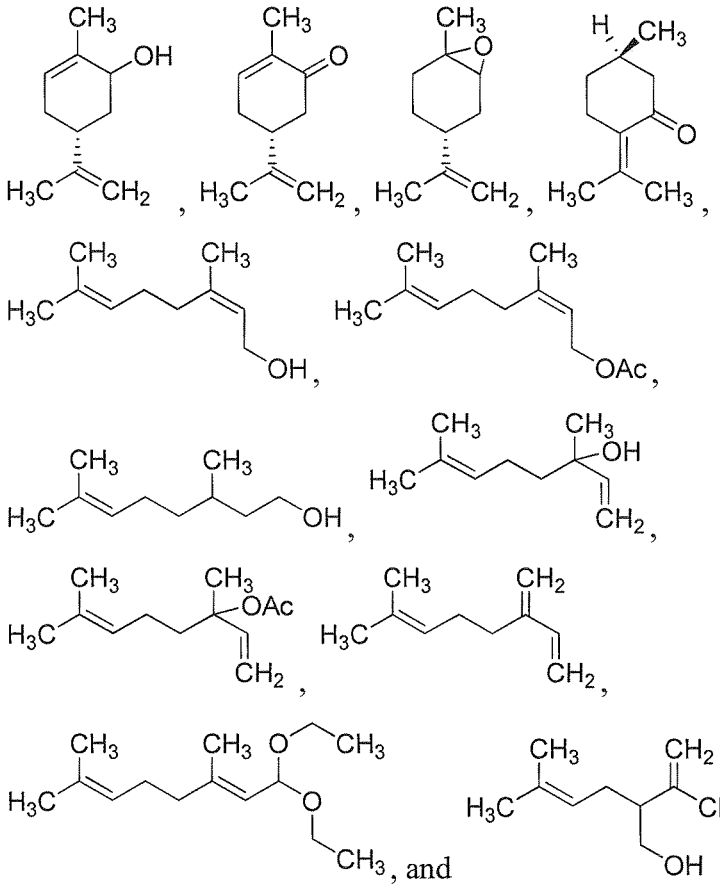
A^1 and A^2 are each, individually at each occurrence, a leaving group or –H, wherein at least one of A^1 and A^2 is a leaving group; and where the leaving group is –Cl, –Br, –I, $–OR^A$, $–OC(O)R^A$, –OTs, or –OMs, where R^A is alkyl having from 1 to 20 carbons;

each X is independently –OH, –F, –Cl, –Br, –I, =O, $–OC(O)R^A$, $–OR^A$, –NC, –NCO, –OCN, –SH, $–SR^A$, $–S(O)R^A$, $–S(O)_2R^A$, –SCN, $–NO_2$, or $–OS(O)_2R^A$, where each R^A is independently alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, or alkynyl having from 2 to 20 carbons, and X is bonded to a primary or secondary carbon; and

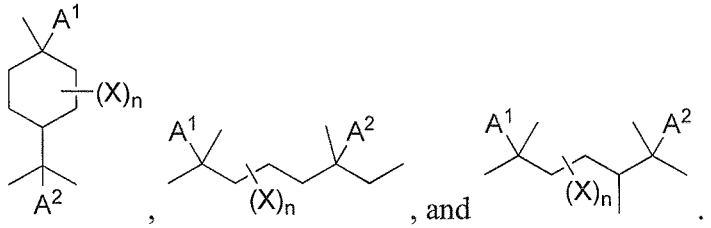
n is an integer from 1 to 3;

(b) , , , , , and ;

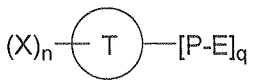
wherein each A^1 and A^2 is independently –Cl, –Br, or –I; and

(c) 

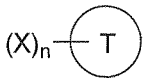
2. The method of claim 1, wherein the terpene initiator is selected from:

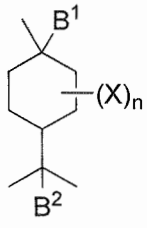


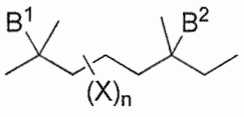
3. The method of claim 1, wherein the telechelic polymer formed has the following formula:

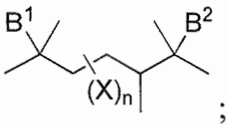


wherein:

 is selected from:



,


, and


;

wherein:

B^1 and B^2, independently at each occurrence, are H or a bond to P, wherein at least one of B^1 and B^2 is a bond to P;

each X is independently –OH, –F, –Cl, –Br, –I, =O, $-OC(O)R^A$, $-OR^A$, –NC, –NCO, –OCN, –SH, $-SR^A$, $-S(O)R^A$, $-S(O)_2R^A$, –SCN, $-NO_2$, or $-OS(O)_2R^A$, wherein each R^A is independently alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, or alkynyl having from 2 to 20 carbons, and X is bonded to a primary or secondary carbon;

each n is independently an integer from 1 to 3;

each P is independently a divalent polyolefin group;

each E is independently an end-cap group; and

q is an integer from 1 to 2.

4. The method of claim 2, wherein X is –OH, $-OR^A$, $-OC(O)R^A$, –F, –Cl, or –Br, wherein R^A is, independently at each occurrence, alkyl of 1-3 carbons.

5. The method of claim 2, wherein X is –OH.

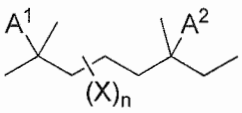
6. The method of claim 2, wherein the leaving group is, independently at each occurrence, –Cl, –Br, –I, or $-OC(O)R^N$, wherein R^N is alkyl having from 1 to 6 carbons.

7. The method of claim 2, wherein n is 1.

8. The method of claim 2, wherein A^1 or A^2 is H.

9. The method of claim 2, wherein X is bonded to a primary carbon.

10. The method of claim 2, wherein the terpene initiator is:



wherein:

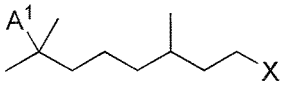
A^1 and A^2 are each individually a leaving group or –H, wherein at least one of A^1 and A^2 is a leaving group; and where the leaving group is –Cl, –Br, –I, $-OR^A$, $-OC(O)R^A$, –OTs, or

–OMs, where R^A is alkyl having from 1 to 20 carbons;

each X is independently –OH, –F, –Cl, –Br, –I, =O, $-OC(O)R^A$, $-OR^A$, –NC, –NCO, –OCN, –SH, $-SR^A$, $-S(O)R^A$, $-S(O)_2R^A$, –SCN, $-NO_2$, or $-OS(O)_2R^A$, where each R^A is independently alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, or alkynyl having from 2 to 20 carbons, and X is bonded to a primary or secondary carbon; and

n is an integer from 1 to 3.

11. The method of claim 10, wherein the terpene initiator is:

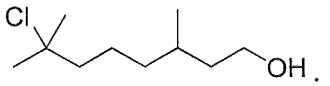


wherein:

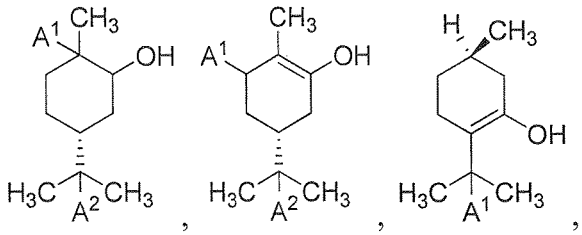
A^1 is a leaving group selected from –Cl, –Br, –I, $-OR^A$, $-OC(O)R^A$, –OTs, or –OMs, where R^A is alkyl having from 1 to 20 carbons; and

X is –OH, –F, –Cl, –Br, –I, =O, $-OC(O)R^A$, $-OR^A$, –NC, –NCO, –OCN, –SH, $-SR^A$, $-S(O)R^A$, $-S(O)_2R^A$, –SCN, $-NO_2$, or $-OS(O)_2R^A$, where each R^A is independently alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, or alkynyl having from 2 to 20 carbons.

12. The method of claim 11, wherein the terpene initiator is:



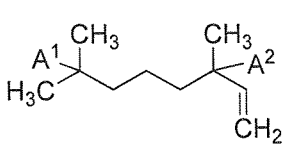
13. The method of claim 1, wherein the terpene initiator is:



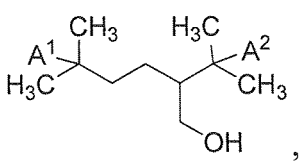
,

,

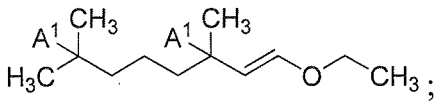
,



,



, or



wherein each A^1 and A^2 is independently –Cl, –Br, or –I.

14. The method of claim 1, further comprising adding one or more quenching agents.

15. The method of claim 14, wherein the quenching agent is:

(a) allyltrimethylsilane;

(b) methallyltrimethylsilane;

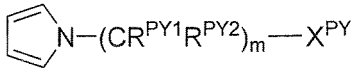
(c) 1,1-diphenylethylene;

(d) furan or a substituted furan;

(e) thiophene or a substituted thiophene;

(f) triphenylamine;

(g) a compound having the following formula:



wherein:

R^{PY1} and R^{PY2} are each independently in each $-(CR^{PY1}R^{PY2})-$ unit selected from the group consisting of hydrogen and alkyl of 1 to 6 carbon atoms;

m is an integer from 1 to 20; and

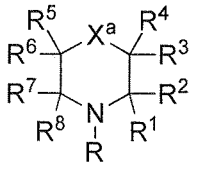
X^{PY} is selected from the group consisting of hydrogen, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, alkaryl having from 7 to 30 carbons, alkoxy having from 1 to 6 carbons, nitro, ureido, $-OC(O)R^{PY3}$, $-C(O)R^{PY4}$, $-C(O)OR^{PY5}$, $-P(R^{PY8})_3$, $-P(OR^{PY9})_3$, $-SR^{PY10}$, $-OSO_3R^{PY11}$, and $-S(O)R^{PY12}$;

wherein:

R^{PY3} is alkyl having from 1 to 20 carbons or alkenyl having from 2 to 20 carbons; and

R^{PY4}, R^{PY5}, R^{PY7}, R^{PY8}, R^{PY9}, R^{PY10}, R^{PY11}, and R^{PY12} are each independently alkyl having from 1 to 20 carbons;

(h) a compound having the following formula:



wherein:

R^1 through R^8 are each independently hydrogen, alkyl from 1 to 20 carbon atoms, aryl from 6 to 30 carbon atoms, alkaryl from 7 to 30 carbon atoms, or aralkyl from 7 to 30 carbon atoms;

R is hydrogen, alkyl from 1 to 20 carbon atoms, aryl from 6 to 30 carbon atoms, alkaryl from 7 to 30 carbon atoms, or aralkyl from 7 to 30 carbon atoms; and

X^a is oxygen or sulfur;

with the proviso that, when R is hydrogen or methyl, then R^1, R^2, R^7 and R^8 must be other than hydrogen unless one of R^1 and R^2 and one of R^7 and R^8 are each independently branched alkyl of 3 to 20 carbon atoms, aryl having from 6 to 30 carbon atoms, alkaryl having from 7 to 30 carbon atoms, or aralkyl having from 7 to 30 carbon atoms;

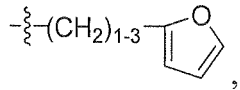
(i) a compound having the following formula:

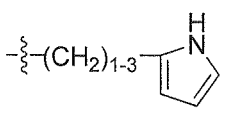
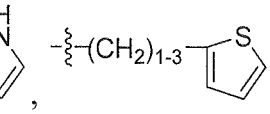
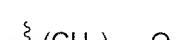
$$R^1\text{–}S\text{–}R^2$$

wherein R^1 and R^2, are each, independently, alkyl having from 1 to 20 carbons;

(j) a compound having the following formula:

$$R^{SA}S\text{–}S\text{–}R^{SB}$$

wherein R^{SA} and R^{SB} are each, independently, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, aralkyl having from 7 to 30 carbons, alkaryl having from 7 to 30 carbons, ,

, , , , or ;

wherein:

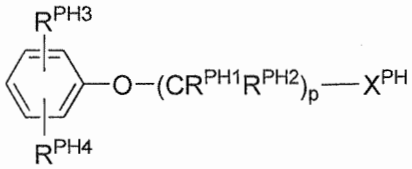
X^S is halo or a pseudohalide;

R^{SX} is alkyl having from 1 to 20 carbons or aryl having from 6 to 30 carbons;

R^{S3} is *tert*-butyl; and

R^{S4} and R^{S5} are each, independently, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, aralkyl having from 7 to 30 carbons, or alkaryl having from 7 to 30 carbons;

(k) a compound having the following formula:

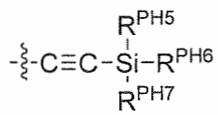


wherein:

R^{PH1} and R^{PH2} are each, independently in each $-(CR^{PH1}R^{PH2})-$ unit, H or alkyl having from 1 to 20 carbons, and p is an integer from 0 to 20, wherein:

(1) if p is 0, then R^{PH3} and R^{PH4} are each, independently, alkyl having from 1 to 20 carbons, and X^{PH} is H;

(2) if p is 1, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, or



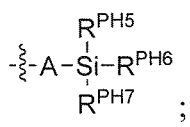
, wherein:

R^{PH5}-R^{PH7} are each, independently, alkyl having from 1 to 20 carbons or aryl having from 6 to 30 carbons;

(3) if p is 2, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, –F, –Cl, –Br, –I, –At, –CN, –NC, –

NCO, –OCN, –NCS,

–SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$, or



;

wherein:

A is $-C\equiv C-$ or a single bond,

R^{PH5} to R^{PH7} are each, independently, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, hydroxy, –$NR^{PH10}R^{PH11}$, –F,

–Cl, –Br, –I, or –At,

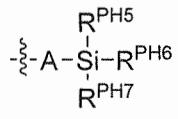
R^{PH8} is alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons, and

R^{PH9} to R^{PH11} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons, or

when $-O-(CR^{PH1}R^{PH2})_p-X^{PH}$ is ortho to R^{PH4}, then X^{PH} and R^{PH4}, together, with the atoms to which X^{PH} and R^{PH4} are attached, form a ring; and

(4) if p is 3-20, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, –OH, –F, –Cl, –Br, –I, –At, –CN, –NC, –NCO, –OCN,

–NCS, –SCN, –$OC(O)R^{PH8}$, –$C(O)OR^{PH9}$, –$C(O)NR^{PH10}R^{PH11}$,



, or –$NR^{PHX}R^{PHY}$;

wherein:

A is  or a single bond,

R^{PHX} and R^{PHY} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, cycloalkyl having from 3 to 7 carbons, aryl having from 6 to 30 carbons, or –$C(O)R^{PHZ}$, wherein R^{PHZ} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, cycloalkyl having from 3 to 7 carbons, aryl having from 6 to 30 carbons,

–OR^{PH8}, or –$NR^{PH10}R^{PH11}$;

R^{PH5} to R^{PH7} are each, independently, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, hydroxy, –$NR^{PH10}R^{PH11}$, –F,

–Cl, –Br, –I, or –At,

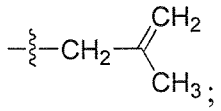
R^{PH8} is alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons, and

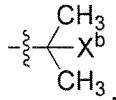
R^{PH9} to R^{PH11} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons;

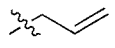
or

(l) butadiene.

16. The method of claim 3, wherein the end-cap group is:

(a) ;

(b) , wherein X^b is a halide;

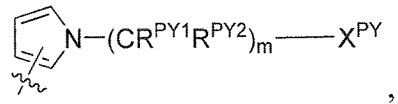
(c) ;

(d) a 1-substituted-1,1-diaryl ethylene group;

(e) furyl or a substituted furyl;

(f) thienyl or a substituted thienyl;

(g) triphenylamino;

(h) ,

wherein:

R^{PY1} and R^{PY2} are independently in each $-(CR^{PY1}R^{PY2})-$ unit selected from the group consisting of hydrogen and alkyl from 1 to 6 carbon atoms;

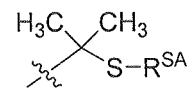
m is an integer from 1 to 20; and

X^{PY} is selected from the group consisting of hydrogen, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, alkaryl having from 7 to 30 carbons, alkoxy having from 1 to 6 carbons, nitro, ureido, $-OC(O)R^{PY3}$, $-C(O)R^{PY4}$, $-C(O)OR^{PY5}$, $-P(R^{PY8})_3$, $-P(OR^{PY9})_3$, $-SR^{PY10}$, $-OSO_3R^{PY11}$, and $-S(O)R^{PY12}$;

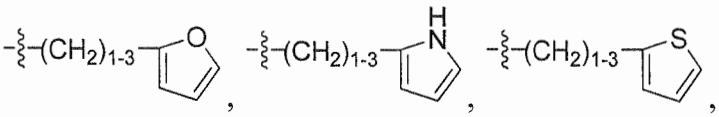
wherein:

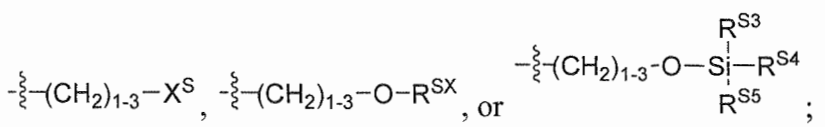
R^{PY3} is alkyl having from 1 to 20 carbons or alkenyl having from 2 to 20 carbons; and

R^{PY4}, R^{PY5}, R^{PY7}, R^{PY8}, R^{PY9}, R^{PY10}, R^{PY11}, and R^{PY12} are each independently alkyl having from 1 to 20 carbons;

(i) ,

wherein R^{SA} is alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, aralkyl having from 7 to 30 carbons, alkaryl having from 7 to 30

carbons, ,

;

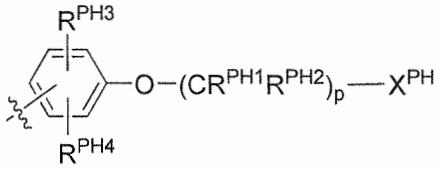
wherein:

X^S is halo or a pseudohalide;

R^{SX} is alkyl having from 1 to 20 carbons or aryl having from 6 to 30 carbons;

R^{S3} is *tert*-butyl; and

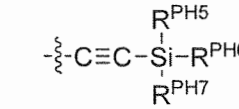
R^{S4} and R^{S5} are each, independently, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, aralkyl having from 7 to 30 carbons, or alkaryl having from 7 to 30 carbons;

(j) ,

wherein:

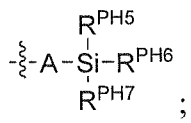
R^{PH1} and R^{PH2} are each, independently in each $-(CR^{PH1}R^{PH2})-$ unit, H or alkyl having from 1 to 20 carbons, and p is an integer from 0 to 20, wherein:

(1) if p is 0, then R^{PH3} and R^{PH4} are each, independently, alkyl having from 1 to 20 carbons, and X^{PH} is H;

(2) if p is 1, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, or , wherein R^{PH5}-R^{PH7} are each, independently, alkyl having from 1 to 20 carbons or aryl having from 6 to 30 carbons;

(3) if p is 2, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6

carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, –F, –Cl, –Br, –I, –At, –CN, –NC, –NCO, –OCN, –NCS,
–SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$, or



;

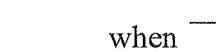
wherein:

A is  or a single bond,

R^{PH5} to R^{PH7} are each, independently, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having 6 from to 20 carbons, alkoxy having from 1 to 6 carbons, hydroxy, $-NR^{PH10}R^{PH11}$, –F,
–Cl, –Br, –I, or –At,

R^{PH8} is alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having 6 from to 20 carbons, and

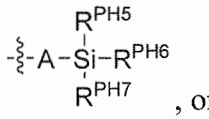
R^{PH9} to R^{PH11} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons, or

when  is ortho to R^{PH4}, then X^{PH} and R^{PH4}, together, with the atoms to which X^{PH} and R^{PH4} are attached, form a ring; and

(4) if p is 3-20, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to

20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, –OH, –F, –Cl, –Br, –I, –At, –CN, –NC, –NCO, –OCN,

–NCS, –SCN, –$OC(O)R^{PH8}$, –$C(O)OR^{PH9}$, –$C(O)NR^{PH10}R^{PH11}$,



, or –$NR^{PHX}R^{PHY}$;

wherein:

A is  or a single bond,

R^{PHX} and R^{PHY} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, cycloalkyl having from 3 to 7 carbons, aryl having from 6 to 30 carbons, or –$C(O)R^{PHZ}$, wherein R^{PHZ} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, cycloalkyl having from 3 to 7 carbons, aryl having from 6 to 30 carbons,

–OR^{PH8}, or –$NR^{PH10}R^{PH11}$;

R^{PH5} to R^{PH7} are each, independently, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, hydroxy, –$NR^{PH10}R^{PH11}$, –F,

–Cl, –Br, –I, or –At,

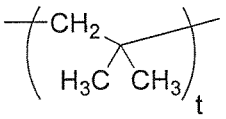
R^{PH8} is alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons, and

R^{PH9} to R^{PH11} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons;

or

(k) allyl.

17. The method of claim 3, wherein P is



wherein t is an integer from 2 to 20,000.

18. The method of claim 1, wherein the one or more monomers is isobutene.

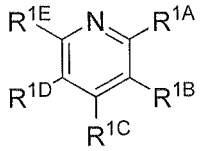
19. The method of claim 1, wherein the one or more monomers is styrene.

20. The method of claim 1, wherein the Lewis acid is a titanium halide, an aluminum halide, a boron halide, or an alkyl aluminum halide.

21. The method of claim 1, wherein the Lewis acid is $TiCl_4$.

22 The method of claim 1, wherein the method is performed in the presence of one or more electron donors.

23. The method of claim 22, wherein the one or more electron donors is:



wherein R^{1A}, R^{1B}, R^{1C}, R^{1D}, and R^{1E} are each, independently, hydrogen or alkyl having from 1 to 20 carbons; or R^{1A} and R^{1B}, or R^{1B} and R^{1C}, or R^{1C} and R^{1D}, or R^{1D} and R^{1E} independently form a fused aliphatic ring of 3 to 7 carbon atoms or a fused aromatic ring of 5 to 7 carbon atoms.

24. The method of claim 23, wherein the one or more electron donors is 2,6-dimethylpyridine, 2,6-di-*tert*-butylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, 2-methylpyridine, or pyridine.

25. The method of claim 1, wherein the method is performed in the presence of a common ion salt precursor selected from *tetra-n*-butylammonium chloride, *tetra-n*-butylammonium bromide, and *tetra-n*-butylammonium iodide.

26. The method of claim 14, wherein greater than 90% of the monomer is consumed prior to adding the one or more quenching agents.

27. The method of claim 14, wherein one or more aliquots of additional monomer are added to the polymerization after the initial monomer charge, wherein each individual aliquot of additional monomer is consumed or partially consumed prior to adding a subsequent aliquot of additional monomer or adding the one or more quenching agents.

28. The method of claim 1, wherein the Lewis acid is deactivated with one or more terminators.

29. The method of claim 14, wherein the Lewis acid is deactivated with one or more terminators after adding the one or more quenching agents.

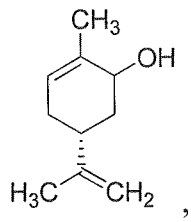
30. The method of claim 3, wherein the Lewis acid is deactivated with one or more terminators and E is a *tert*-halide.

31. The method of claim 1, wherein the telechelic polyolefin has a polydispersity index of less than 1.9.

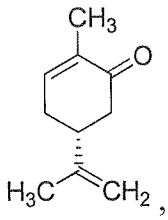
32. The method of claim 1, wherein the monomer is polymerized under quasiliving polymerization conditions.

33. The method of claim 1, wherein the terpene initiator is derived by hydrohalogenation of a unsaturated terpene.

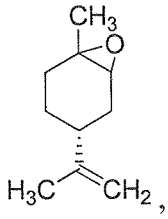
34. The method of claim 1, wherein the terpene initiator is derived from a compound selected from:



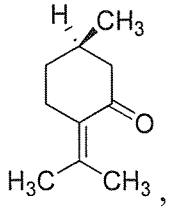
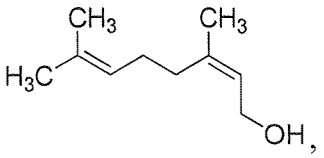
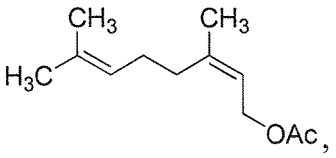
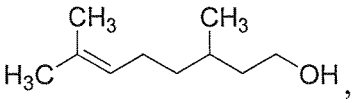
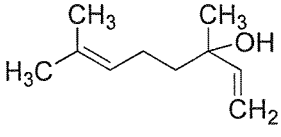
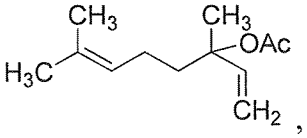
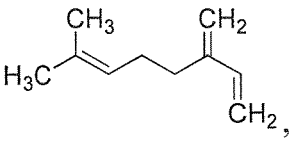
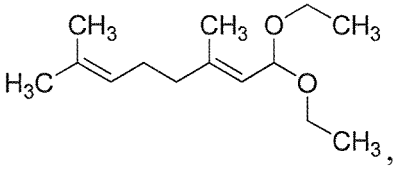
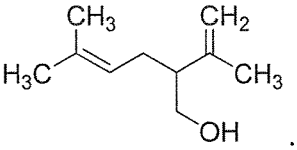
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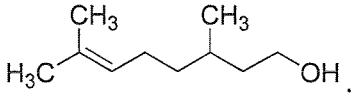
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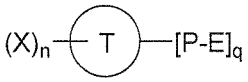
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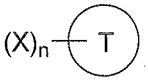
35. The method of claim 34, wherein the terpene initiator is derived from:

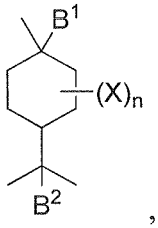
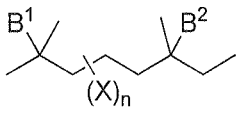
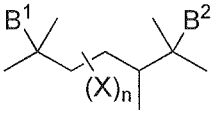


36. A compound having the following formula:



wherein:


is selected from:

(a) , , and ;

wherein:

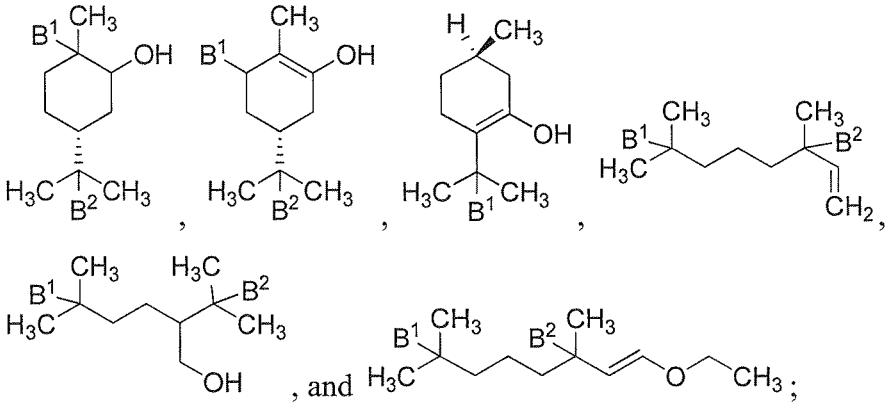
B^1 and B^2, independently at each occurrence, are H or a bond to P, wherein at least one of B^1 and B^2 is a bond to P;

each X is independently –OH, –F, –Cl, –Br, –I, –NC, –NCO, –OCN, –SH, $-SR^A$, $-S(O)R^A$, $-S(O)_2R^A$, –SCN, $-OR^A$, $-NO_2$, $-OS(O)_2R^A$, =O, or $-OC(O)R^A$, wherein each R^A is independently alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20

carbons, or alkynyl having from 2 to 20 carbons, and X is bonded to a primary or secondary carbon;

each n is independently an integer from 1 to 3;

and

(b) 

wherein each B^1 and B^2 is independently H or a bond to P; and at least one of B^1 and B^2 is a bond to P;

each P is independently a divalent polyolefin group;

each E is independently an end-cap group; and

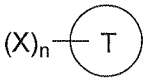
q is an integer from 1 to 2.

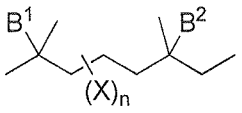
37. The compound of claim 37, wherein X is –OH, $-OR^A$, $-OC(O)R^A$, –F, –Cl, or –Br, wherein R^A is, independently at each occurrence, alkyl of 1-3 carbons.

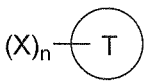
38. The compound of claim 37, wherein n is 1.

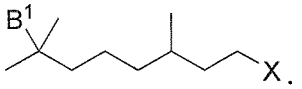
39. The compound of claim 37, wherein X is bonded to a primary carbon.

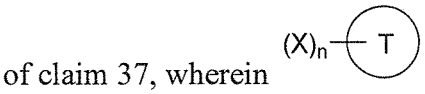
40. The compound of claim 37, wherein X is bonded to a secondary carbon.

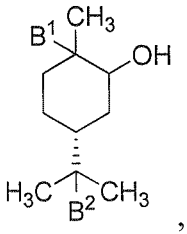
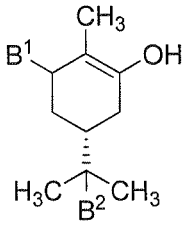
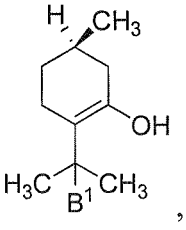
41. The compound of claim 37, wherein  is:

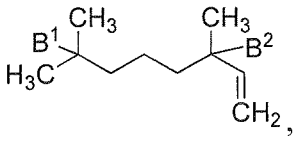
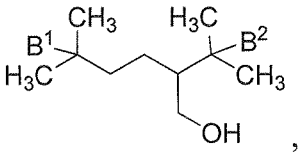
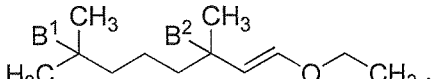


42. The compound of claim 37, wherein  is:



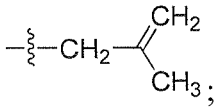
43. The compound of claim 37, wherein  is

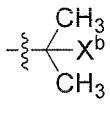
, , ,

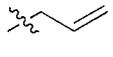
, , or ;

wherein B^1 and B^2 are each independently H or a bond to P; and at least one of B^1 and B^2 is a bond to P.

44. The compound of claim 37, wherein the end-cap group is:

(a) ;

(b) , wherein X^b is a halide;

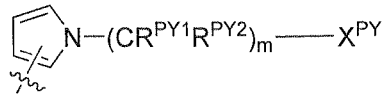
(c) ;

(d) a 1-substituted-1,1-diaryl ethylene group;

(e) furyl or a substituted furyl;

(f) thienyl or a substituted thienyl;

(g) triphenylamino;

(h) ,

wherein:

R^{PY1} and R^{PY2} are independently in each $-(CR^{PY1}R^{PY2})-$ unit selected from the group consisting of hydrogen and alkyl from 1 to 6 carbon atoms;

m is an integer from 1 to 20; and

X^{PY} is selected from the group consisting of hydrogen, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, alkaryl having from 7 to 30 carbons, alkoxy having from 1 to 6 carbons, nitro, ureido, $-OC(O)R^{PY3}$,

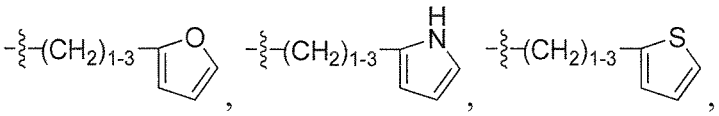
$-C(O)R^{PY4}$, $-C(O)OR^{PY5}$, $-P(R^{PY8})_3$, $-P(OR^{PY9})_3$, $-SR^{PY10}$, $-OSO_3R^{PY11}$, and $-S(O)R^{PY12}$;

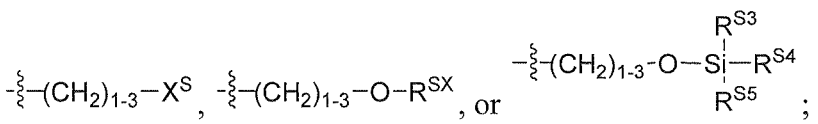
wherein:

R^{PY3} is alkyl having from 1 to 20 carbons or alkenyl having from 2 to 20 carbons; and

R^{PY4}, R^{PY5}, R^{PY7}, R^{PY8}, R^{PY9}, R^{PY10}, R^{PY11}, and R^{PY12} are each independently alkyl having from 1 to 20 carbons;

(i) ,

wherein R^{SA} is alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, aralkyl having from 7 to 30 carbons, alkaryl having from 7 to 30 carbons, ,

;

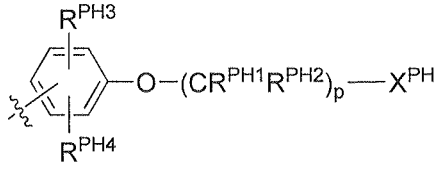
wherein:

X^S is halo or a pseudohalide;

R^{SX} is alkyl having from 1 to 20 carbons or aryl having from 6 to 30 carbons;

R^{S3} is *tert*-butyl; and

R^{S4} and R^{S5} are each, independently, alkyl having from 1 to 20 carbons, aryl having from 6 to 30 carbons, aralkyl having from 7 to 30 carbons, or alkaryl having from 7 to 30 carbons;

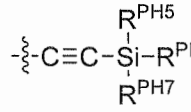
(j) ,

wherein:

R^{PH1} and R^{PH2} are each, independently in each $-(CR^{PH1}R^{PH2})-$ unit, H or alkyl having from 1 to 20 carbons, and p is an integer from 0 to 20, wherein:

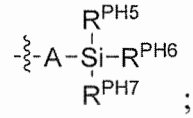
(1) if p is 0, then R^{PH3} and R^{PH4} are each, independently, alkyl having from 1 to 20 carbons, and X^{PH} is H;

(2) if p is 1, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, or



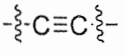
, wherein R^{PH5}-R^{PH7} are each, independently, alkyl having from 1 to 20 carbons or aryl having from 6 to 30 carbons;

(3) if p is 2, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X^{PH} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, –F, –Cl, –Br, –I, –At, –CN, –NC, –NCO, –OCN, –NCS,
–SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$, or



;

wherein:

A is  or a single bond,

R^{PH5} to R^{PH7} are each, independently, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, hydroxy, –$NR^{PH10}R^{PH11}$, –F,
–Cl, –Br, –I, or –At,

R^{PH8} is alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20

carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons, and

R^{PH9} to R^{PH11} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 2 to 20 carbons, or aryl having from 6 to 30 carbons, or

when $-O-(CR^{PH1}R^{PH2})_p-X^{PH}$ is ortho to R^{PH4}, then X^{PH} and R^{PH4}, together, with the atoms to which X^{PH} and R^{PH4} are attached, form a ring; and

(4) if p is 3-20, then R^{PH3} and R^{PH4} are each, independently H, alkyl having from 1 to 20 carbons, or alkoxy having from 1 to 6 carbons, and X is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, –OH, –F, –Cl, –Br, –I, –At, –CN, –NC, –NCO, –OCN,

–NCS, –SCN, $-OC(O)R^{PH8}$, $-C(O)OR^{PH9}$, $-C(O)NR^{PH10}R^{PH11}$,

, or $-NR^{PHX}R^{PHY}$;

wherein:

A is or a single bond,

R^{PHX} and R^{PHY} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, cycloalkyl having from 3 to 7 carbons, aryl having from 6 to 30 carbons, $-C(O)R^{PHZ}$, wherein R^{PHZ} is H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, cycloalkyl having from 3 to 7 carbons, aryl having from 6 to 30 carbons,

$-OR^{PH8}$, or $-NR^{PH10}R^{PH11}$;

R^{PH5} to R^{PH7} are each, independently, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl

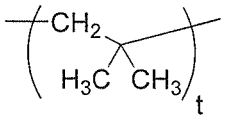
having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, aralkyl having from 7 to 30 carbons, aryl having from 6 to 30 carbons, alkoxy having from 1 to 6 carbons, hydroxy, $-NR^{PH10}R^{PH11}$, –F, –Cl, –Br, –I, or –At, R^{PH8} is alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 2 to 20 carbons, or aryl having from 6 to 30 carbons, and

R^{PH9} to R^{PH11} are each, independently, H, alkyl having from 1 to 20 carbons, alkenyl having from 2 to 20 carbons, alkynyl having from 2 to 20 carbons, alkaryl having from 7 to 30 carbons, or aryl having from 6 to 30 carbons;

or

(k) allyl.

45. The compound of claim 37, wherein P is



wherein t is an integer from 2 to 20000.

46. The compound of claim 37, wherein the compound has a polydispersity index of less than 1.9.