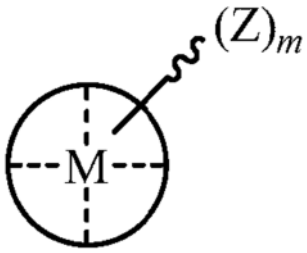
CLAIMS

What is claimed is:

1. A metal complex of the formula:

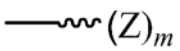


,

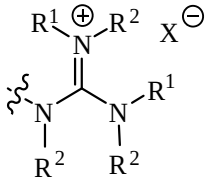
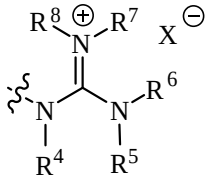
wherein:

M is cobalt;

 comprises a salen ligand; and

 represents one or more activating moieties tethered to the salen ligand, where represents a linker moiety;

m is an integer between 1 and 4 inclusive and represents the number of Z groups present on a linker moiety; and

each (Z) represents an activating moiety comprising a guanidinium group according to formula  or ,

wherein

X^- is an anion;

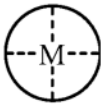
each occurrence of R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic, C_{1-20} heteroaliphatic; phenyl, a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially

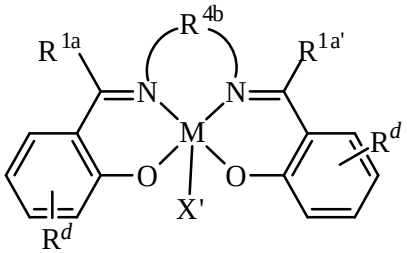
unsaturated or aromatic polycyclic carbocycle, a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein two or more R^1 and R^2, groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms, and

each of R^4, R^5, R^6, R^7, and R^8 is independently hydrogen or C_{1-20} aliphatic, where any of (R^4 and R^5), (R^5 and R^6), (R^6 and R^7), (R^7 and R^8), and (R^4 and R^7) can be taken together with intervening atoms to form rings.

2. The metal complex of claim 1, wherein one or more of R^4, R^5, R^6, and R^7, is optionally substituted C_{1-12} aliphatic.

3. The metal complex of claim 1, wherein (R^4 and R^5) and (R^6 and R^7) are taken together to form rings.

4. The metal complex of claim 3, wherein  comprises:

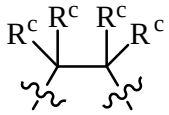


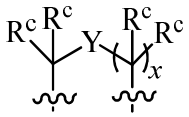
, where

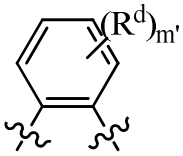
R^{1a} and $R^{1a'}$ are independently a $\text{—}\sim\sim(Z)_m$ group, hydrogen, or an optionally substituted radical selected from the group consisting of: C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen and sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 atoms independently selected from nitrogen, oxygen and sulfur; and a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms selected from nitrogen, oxygen and sulfur;

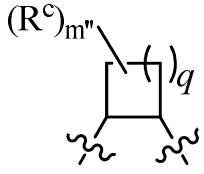
R^d at each occurrence is independently a $\text{—}\sim\sim(Z)_m$ group, hydrogen, halogen, -OR, $-NR_2$, -SR, -CN, $-NO_2$, $-SO_2R$, -SOR, $-SO_2NR_2$; -CNO, $-NRSO_2R$, -NCO, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^d groups may be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms,

R^{4b} is selected from the group consisting of:

a) ;

b)  ;

c)  ; and

d)  , where

R^c at each occurrence is independently a group, hydrogen, halogen, -OR, -NR_2, -SR, -CN, -NO_2, -SO_2R, -SOR, -SO_2NR_2; -CNO, -NRSO_2R, -NCO, -N_3, -SiR_3; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^c groups may be taken together with the carbon atoms to which they are attached and any intervening atoms to form one or more optionally substituted rings; when two R^c groups are attached to the same carbon atom, they may optionally be taken together along with the carbon atom to which they are attached to form an optionally substituted moiety selected from the group consisting of: a 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, and an imine;

Y is a divalent linker selected from the group consisting of: -NR-, -N(R)C(O)-, -C(O)NR-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, -SO_2-, -SiR_2-, -C(=S)-, -C(=NR)-, or -N=N-; a polyether; a C_3 to C_8 substituted or unsubstituted carbocycle; and a C_1 to C_8 substituted or unsubstituted heterocycle;

R at each occurrence is independently hydrogen, an optionally substituted radical selected from the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring,

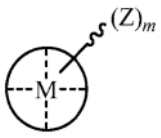
X′ is a nucleophile capable of ring opening an epoxide;

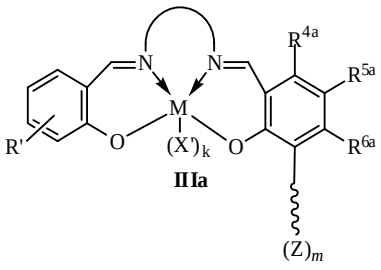
m′ is 0 or an integer from 1 to 4, inclusive;

m″ is 0 or an integer from 1 to 6, inclusive;

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

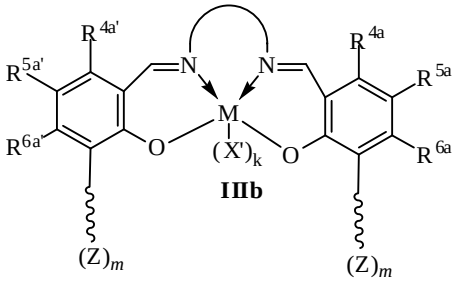
x is 0, 1, or 2.

5. The metal complex of claim 3, wherein , is selected from the group consisting of:



IIIa

and



IIIb

,

where  represents an optionally substituted moiety linking the two nitrogen atoms, and is selected from the group consisting of: phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an optionally substituted C_{2-20} aliphatic group, wherein one or more methylene units are optionally and independently replaced by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-OC(O)N(R^y)-$, $-N(R^y)C(O)O-$, $-OC(O)O-$, $-O-$, $-C(O)-$, $-OC(O)-$, $-C(O)O-$, $-S-$, $-SO-$, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, $-C(=NOR^y)-$or $-N=N$;

R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ are each independently a group, hydrogen,

halogen, $-OR$, $-NR_2$, $-SR$, $-CN$, $-NO_2$, $-SO_2R$, $-SOR$, $-SO_2NR_2$; $-CNO$, $-NRSO_2R$, $-NCO$, $-N_3$, $-SiR_3$; or an optionally substituted radical selected

from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two adjacent R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings,

R' represents one or more substituents optionally present on the phenyl ring and each R' is independently selected from the group consisting of: halogen, $-NO_2$, -CN, $-SR^y$, $-S(O)R^y$, $-S(O)_2R^y$, $-NR^yC(O)R^y$, $-OC(O)R^y$, $-CO_2R^y$, -NCO, $-N_3$, $-OR^7$, $-OC(O)N(R^y)_2$, $-N(R^y)_2$, $-NR^yC(O)R^y$, $-NR^yC(O)OR^y$; and an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur, where two or more adjacent R' groups can be taken together to form

an optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms;

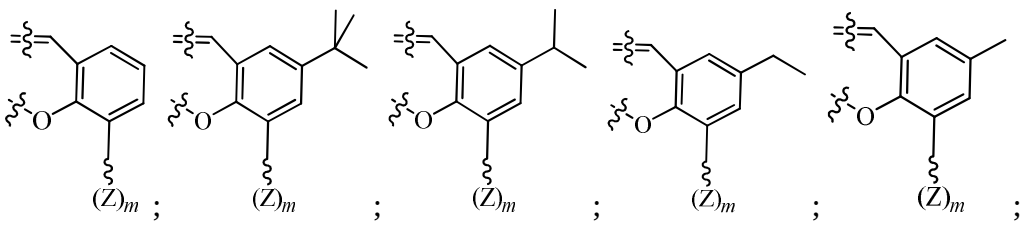
R at each occurrence is independently hydrogen, an optionally substituted radical selected from the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring,

R^y is -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl;

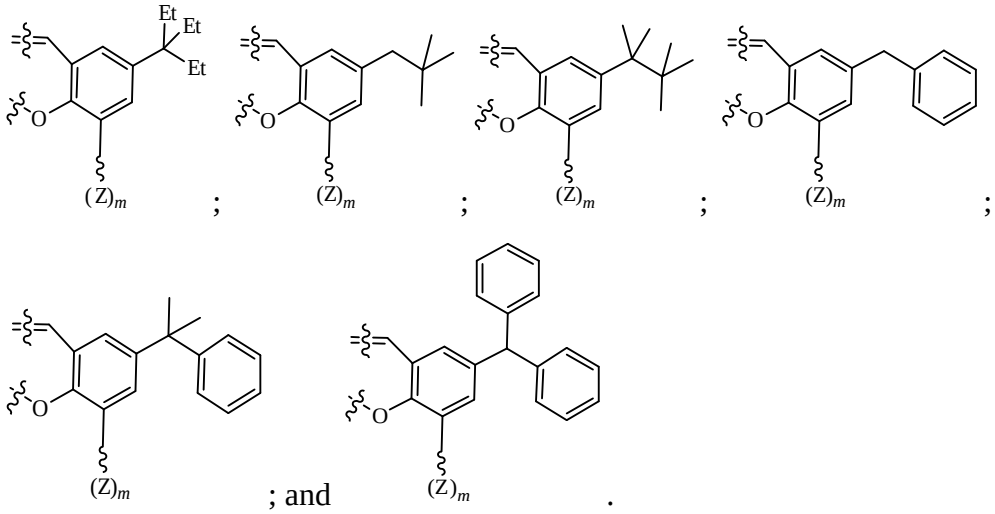
X′ is a nucleophile capable of ring opening an epoxide; and

k is 1.

6. The metal complex of claim 5, wherein the metal complex comprises a substructure conforming to a formula selected from the group consisting of:



;



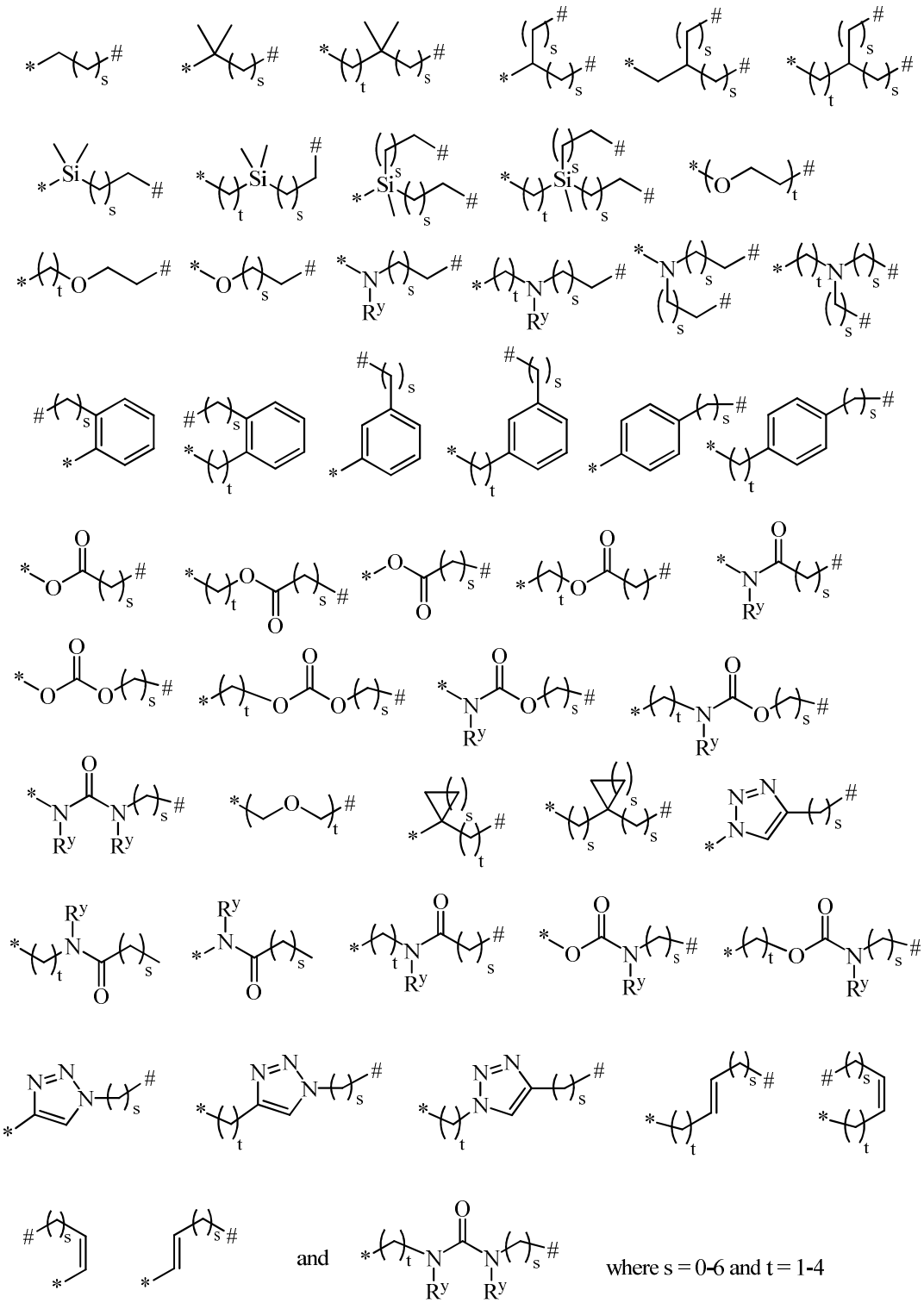
; and .

7. The metal complex of claim 6, wherein ——〰 comprises a C_{3-30} aliphatic group.

8. The metal complex of claim 7, wherein ——〰 comprises a C_{4-8} aliphatic group.

9. The metal complex of claim 7, wherein ——〰 comprises a C_3 aliphatic group.

10. The metal complex of claim 6, wherein ——〰 is selected from the group consisting of:



,

where * represents the site of attachment to the ligand, and each # represents a site of attachment to the guanidinium activating moiety.

11. The metal complex of claim 4, wherein X´is selected from the group consisting of: chlorine, bromine, an optionally substituted C_{1-12} carboxylate, azide, an optionally substituted phenoxide, and sulfonate.

12. The metal complex of claim 11, wherein X´ is selected from the group consisting of: chloride, acetate, trifluoroacetate, azide, pentafluorobenzoate, and a nitrophenolate.

13. A method for the synthesis of aliphatic polycarbonate polymers comprising the step of contacting one or more epoxides with carbon dioxide in the presence of a metal complex of claim 1.

14. The method of claim 13, wherein the epoxide is selected from the group consisting of: ethylene oxide, propylene oxide, butylene oxide, cyclohexene oxide, 1,2 octene oxide, 3-vinyl cyclohexene oxide, epichlorohydrin and mixtures of any two or more of these.

15. The method of claim 14, wherein the epoxide is ethylene oxide, propylene oxide, or cyclohexene oxide.

16. The method of claim 13, wherein the epoxide is ethylene oxide.

17. The method of claim 13, wherein the epoxide is propylene oxide.

18. The method of claim 13, wherein a pressure of carbon dioxide is between 50 and 800 psi.