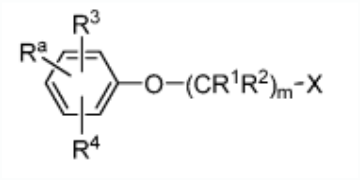
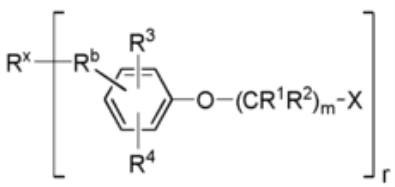
[0004a] According to an aspect there is provided a method for preparing a compound of formula I:



I;

or the formula



wherein

R^a is a polyolefin group;

R^1 and R^2 are each, independently in each -(CR^1R^2) unit, H or alkyl;

R^b is a polyisobutylene group;

R^X is a polyfunctional carbocationic initiator residue;

R is an integer from 1 to 4; and

m is an integer from 0 to 20; wherein

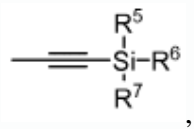
if m is 0,

then R^3 and R^4 are each, independently, alkyl, and X is H;

if m is 1,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl or



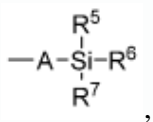
,

wherein R^5 -R^7 are each, independently, alkyl or aryl;

if m is 2,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, -$OC(O)R^8$, -$C(O)OR^9$, -$C(O)NR^{10}R^{11}$,



,

wherein A is  or nothing,

R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, -$NR^{10}R^{11}$, -F, -Cl, -Br, -I, or -At,

R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

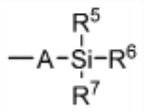
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl,

or, when -O-$(CR^1R^2)_m$-X is ortho to R^4 then X and R^4, together, with the atoms to which X and R^4 are attached, may form a ring;

and if m is 3-20,

then R^3 and R^4 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, -$OC(O)R^8$, -$C(O)OR^9$, $C(O)NR^{10}R^{11}$,



,

or $-NR^XR^Y$;

wherein A is or nothing,

R^X and R^Y are each, independently, H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, $C(O)R^Z$,

wherein R^Z is H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, -OR^8, or $NR^{10}R^{11}$;

R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, -$NR^{10}R^{11}$, -F, -Cl, -Br, -I, or -At,

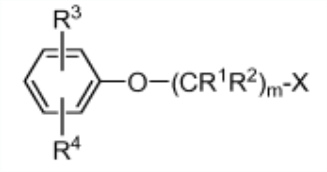
R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl;

comprising:

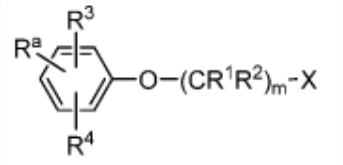
(a) generating a quasiliving carbocationic polyolefin; and

(b) reacting the quasiliving carbocationic polyolefin from step (a) with one or more compounds of formula II in the presence of a Lewis acid or mixture of Lewis acids under quasiliving carbocationic polymerization conditions:



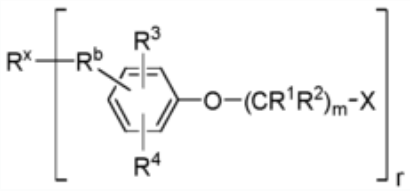
II.

[0004b] According to another aspect there is provided a compound of formula I:



I

or the formula



wherein

R^a is a polyolefin group;

R^1 and R^2 are each, independently in each -(CR^1R^2) unit, H or alkyl;

R^b is a polyisobutylene group;

R^X is a polyfunctional carbocationic initiator residue;

R is an integer from 1 to 4; and

m is an integer from 1 to 20; wherein

if m is 0,

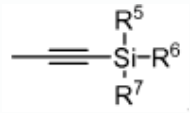
then R^3 and R^4 are each, independently, alkyl, and

X is H;

if m is 1 and at least one of R^3 and R^4 is not H,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl or



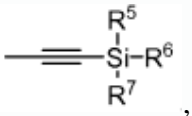
,

wherein R^5-R^7 are each, independently, alkyl or aryl;

if m is 1 and R^3 and R^4 are both H,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, or

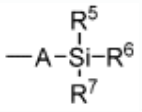

,

wherein R^5-R^7 are each, independently, alkyl or aryl;

if m is 2,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, -$OC(O)R^8$, -$C(O)OR^9$, -$C(O)NR^{10}R^{11}$,


,

wherein R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, or hydroxy,

R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

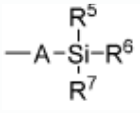
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl,

or, when –O-$(CR^1R^2)_m$-X is ortho to R^4, X and R^4 together, with the atoms to which X and R^4 are attached, may form a ring;

and if m is 3-20,

then R^3 and R^4 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, -$OC(O)R^8$, -$C(O)OR^9$, -$C(O)NR^{10}R^{11}$,


,

or -NR^XR^Y;

wherein R^X and R^Y are each, independently, H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, $C(O)R^Z$,

wherein R^Z is H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, -OR, or $-NR^{10}R^{11}$;

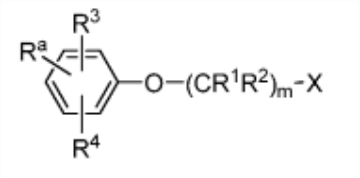
R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, or hydroxy,

R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl.

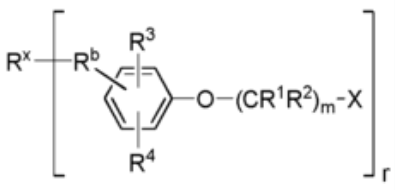
WHAT IS CLAIMED:

1. A method for preparing a compound of formula I:



I;

or the formula



wherein

R^a is a polyolefin group;

R^1 and R^2 are each, independently in each $-(CR^1R^2)$ unit, H or alkyl;

R^b is a polyisobutylene group;

R^X is a polyfunctional carbocationic initiator residue;

R is an integer from 1 to 4; and

m is an integer from 0 to 20; wherein

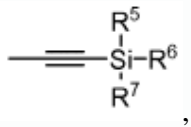
if m is 0,

then R^3 and R^4 are each, independently, alkyl, and X is H;

if m is 1,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl or



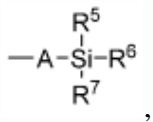
,

wherein R^5 -R^7 are each, independently, alkyl or aryl;

if m is 2,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, $-OC(O)R^8$, $-C(O)OR^9$, $-C(O)NR^{10}R^{11}$,



,

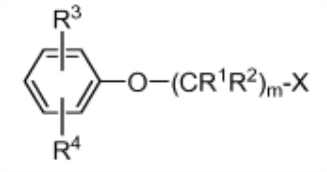
wherein A is or nothing,

R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl;

comprising:

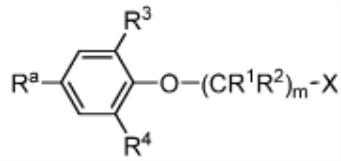
(a) generating a quasiliving carbocationic polyolefin; and

(b) reacting the quasiliving carbocationic polyolefin from step (a) with one or more compounds of formula II in the presence of a Lewis acid or mixture of Lewis acids under quasiliving carbocationic polymerization conditions:

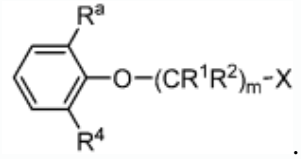


II.

2. The method of claim 1, wherein the compound of formula I is:



or wherein the compound of formula I is:



.

3. The method of claim 1, wherein R^a is a polyisobutyl group.

4. The method of claim 1 , wherein the method is performed in the presence of a mono-functional, bi- functional, or multi-functional initiator.

5. The method of claim 1, wherein:

R^1 and R^2 are both H; or

R^1 and R^2 are each, independently in each -(CR^1R^2) unit, alkyl of 1 to 6 carbons or hydrogen; or

R^1 and R^2 are each, independently in each -(CR^1R^2) unit, methyl or hydrogen; or

R^3 and R^4 are identical;

m is 1-20 and R^3 and R^4 are hydrogen; or

R^3 and R^4 are each, independently, tert-butyl; or

m is 0; or

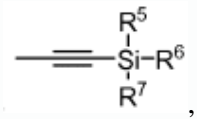
m is 1; or

m is 2; or

m is 3-20; or

m is 1 and X is H, alkyl of 1 to 6 carbons, or alkenyl of 2 to 6 carbons; or

m is 1 and X is



,

optionally wherein at least one of R^5-R^7 is tert-butyl, or wherein at least one of R^5-R^7 is phenyl; or m is 2-20 and X is H, alkyl of 1 to 6 carbons, alkenyl of 2 to 6 carbons, F, Cl, Br, or I; or

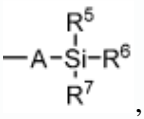
m is 2-20 and X is Cl, or Br; or

m is 3 to 20 and X is OH; or

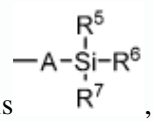
R^8-R^{11} are each, independently, alkyl of 1 to 6 carbons; or

m is 2; R^1 and R^2 are H; -O-$(CR^1R^2)_m$-X is ortho to R^4; and X and R^4, together, with the atoms to which X and R^4 are attached, form a ring; or

m is 2 and X is

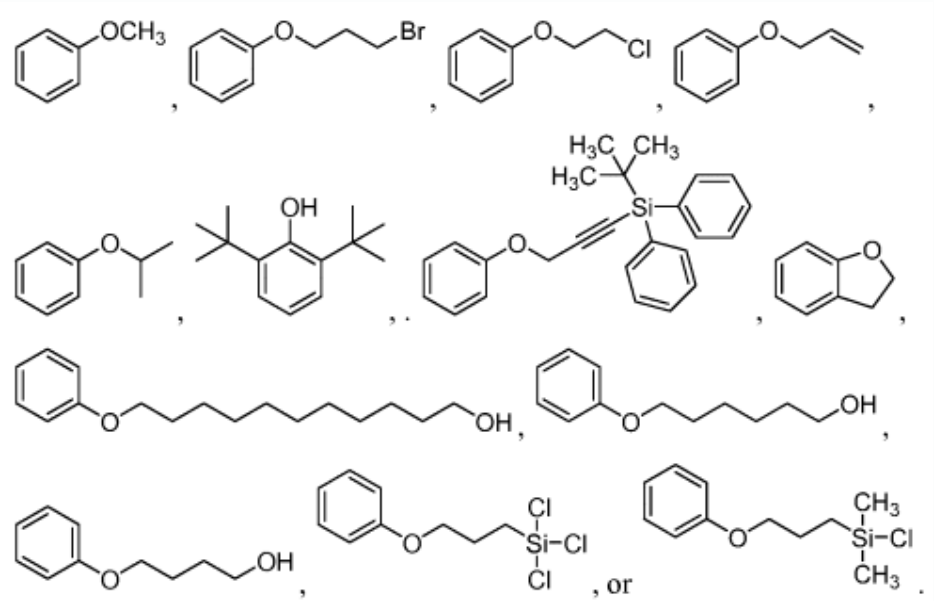


,

optionally wherein at least one of R^5-R^7 is tert-butyl, or wherein at least one of R^5-R^7 is phenyl; or m is 3-20 and X is ,

optionally wherein at least one of R^5-R^7 is tert-butyl, or wherein at least one of R^5-R^7 is phenyl.

6. The method of claim 1, wherein the compound of formula II is



, or .

7. The method of claim 1, wherein the quasiliving carbocationic polyolefin is prepared by adding a Lewis acid and a monomer to an initiator in the presence of an electron donor, common ion salt, or common ion salt precursor.

8. The method of claim 7, wherein the initiator is mono functional (for example 2-chloro-2,4,4-trimethylpentane), or wherein the initiator is bifunctional (for example 5-tert-butyl-l,3-bis(l-chloro-1-methylethyl)benzene) or wherein the initiator is multifunctional (for example l,3,5-tri(2-chloro-2-propyl)benzene or l,3,5-tri(2-methoxy-2-propyl)benzene).

9. The method of claim 7, wherein the monomer is isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, or 4-methyl-l-pentene, or wherein the monomer is isobutylene.

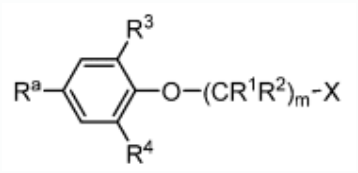
10. The method of claim 7, wherein the electron donor is 2,6-dimethylpyridine; or

the common ion salt precursor is tetrabutylammonium chloride or tetrabutylammonium iodide; or

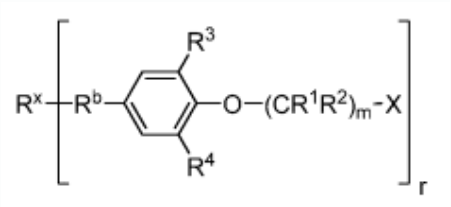
the Lewis acid is a titanium tetrahalide, a boron trihalide, aluminum trichloride, tin tetrachloride, zinc chloride, or ethyl aluminum dichloride, or mixtures thereof; or the Lewis acid is titanium tetrachloride; or a mixture of Lewis acids is used.

11. The method of claim 1, wherein a diluent is used.

12. The method of claim 1, wherein

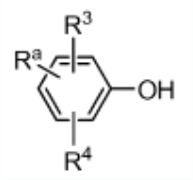


is the major isomer product, or wherein



is the major isomer product.

13. The method of claim 1, further comprising a step of reacting the compound of formula I with an acid to form a compound of formula III:

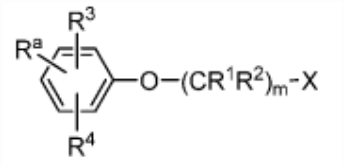


III.

14. The method of claim 13, wherein the acid is a Lewis acid, wherein the Lewis acid is a metal halide or a mixture of metal halides; or wherein the acid is BBr_3, BCl_3, $AlCl_3$, $AlBr_3$, $TiCl_4$, or $TiBr_4$ or wherein the acid is BBr_3.

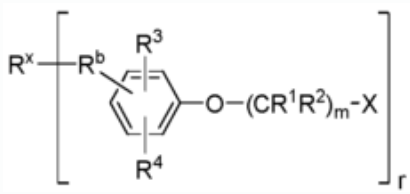
15. The method of claim 14, wherein the Lewis acid is used in conjunction with a protic acid, wherein the protic acid is optionally selected from H_2SO_4, HBr, HCl, trifluoroacetic acid, para-toluenesulfonic acid, or methanesulfonic acid.

16. A compound of formula I:



I

or the formula



wherein

R^a is a polyolefin group;

R^1 and R^2 are each, independently in each -(CR^1R^2) unit, H or alkyl;

R^b is a polyisobutylene group;

R^X is a polyfunctional carbocationic initiator residue;

R is an integer from 1 to 4; and

m is an integer from 1 to 20; wherein

if m is 0,

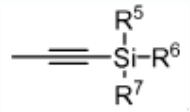
then R^3 and R^4 are each, independently, alkyl, and

X is H;

if m is 1 and at least one of R^3 and R^4 is not H,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl or



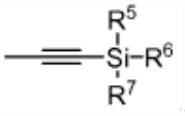
,

wherein R^5-R^7 are each, independently, alkyl or aryl;

if m is 1 and R^3 and R^4 are both H,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, or

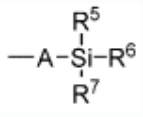

,

wherein R^5-R^7 are each, independently, alkyl or aryl;

if m is 2,

then R^3 and R^4 are each, independently, H, alkyl, or alkoxy, and

X is H, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, -F, -Cl, -Br, -I, -At, -CN, -NC, -NCO, -OCN, -NCS, -SCN, -$OC(O)R^8$, -$C(O)OR^9$, -$C(O)NR^{10}R^{11}$,


,

wherein R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, or hydroxy,

R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

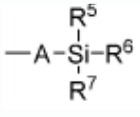
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl,

or, when –O-$(CR^1R^2)_m$-X is ortho to R^4, X and R^4 together, with the atoms to which X and R^4 are attached, may form a ring;

and if m is 3-20,

then R^3 and R^4 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, -$OC(O)R^8$, -$C(O)OR^9$, -$C(O)NR^{10}R^{11}$,


,

or -NR^XR^Y;

wherein R^X and R^Y are each, independently, H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, $C(O)R^Z$,

wherein R^Z is H, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, heteroaryl, heterocyclyl, -OR, or $-NR^{10}R^{11}$;

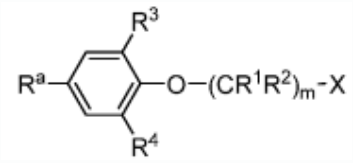
R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, or hydroxy,

R^8 is alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl, and

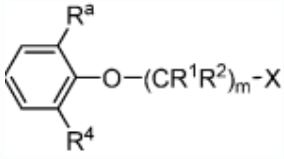
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl.

17. The compound of claim 16, wherein the polyolefin group is a polyisobutyl group.

18. The compound of claim 16, wherein the compound:

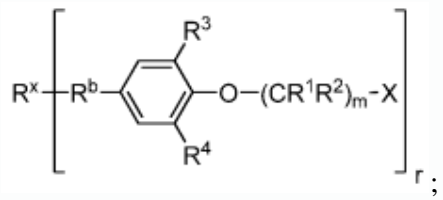


or wherein the compound is



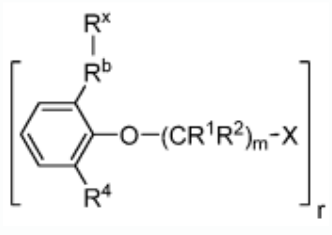
.

19. The method of claim 4 or the compound of claim 16, wherein the compound is:



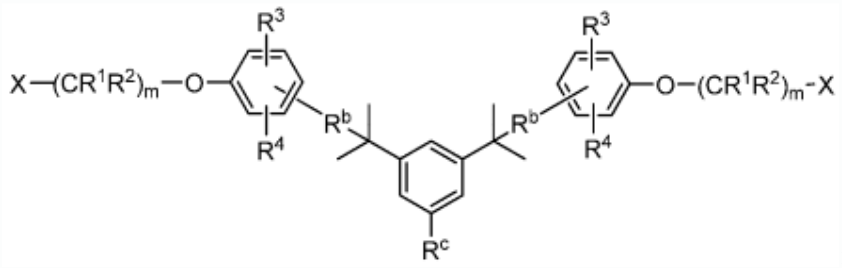
;

or wherein the compound is:



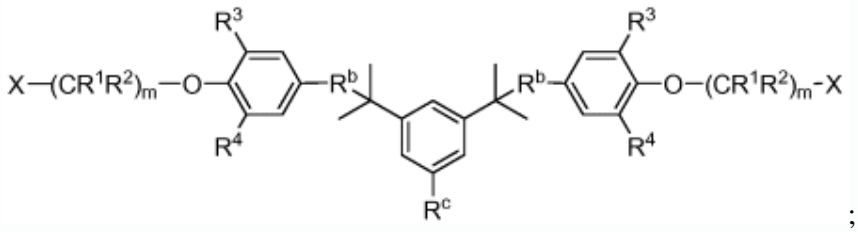
;

or wherein the compound is:



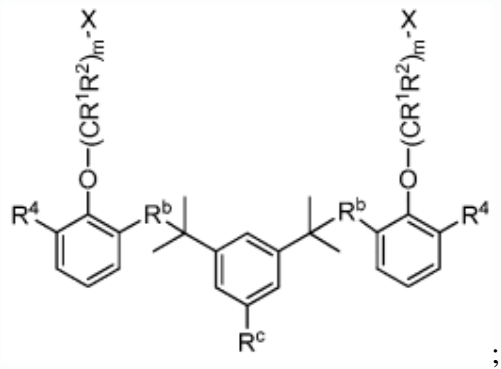
;

wherein R^c is H or alkyl, optionally wherein R^c is alkyl of 1 to 6 carbons; or wherein the compound is:



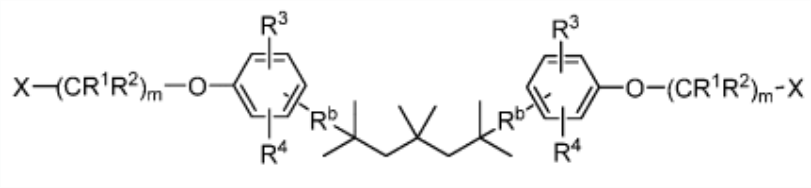
;

or wherein the compound is:



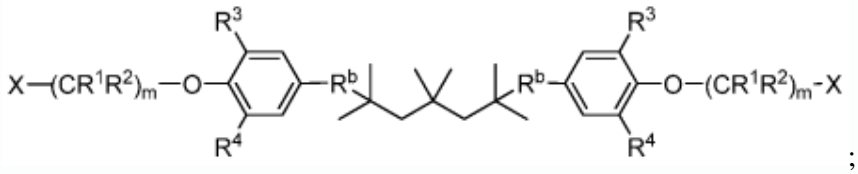
;

or wherein the compound is:



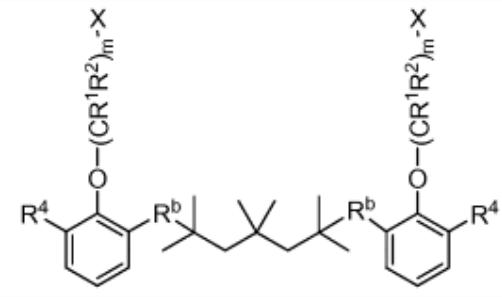
;

or wherein the compound is:



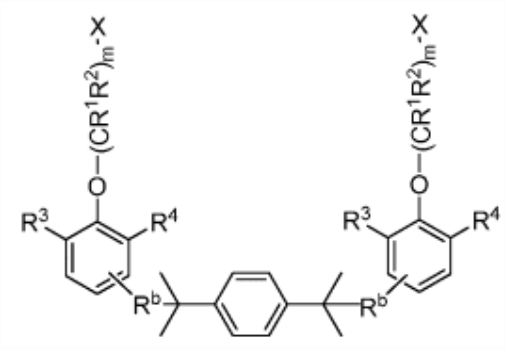
;

or wherein the compound is:



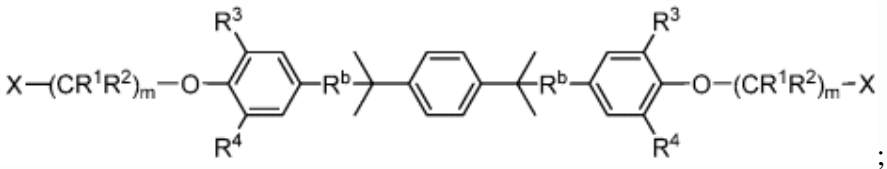
;

or wherein the compound is:



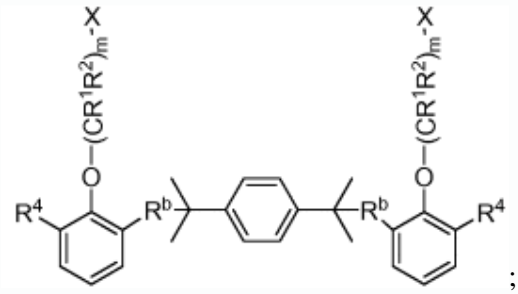
;

or wherein the compound is:



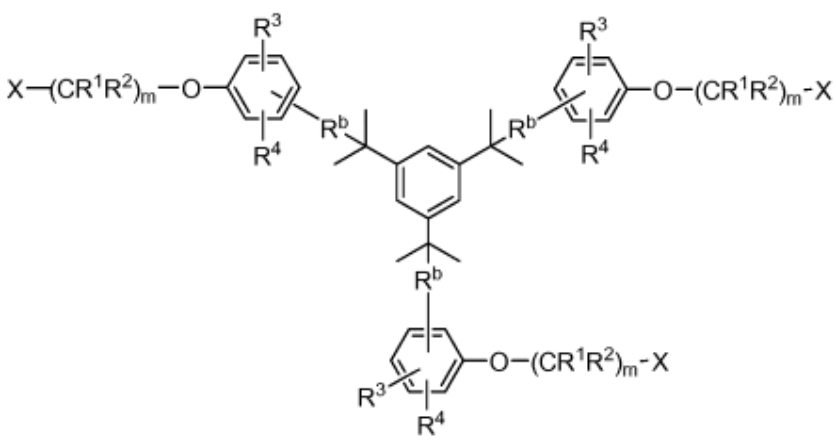
;

or wherein the compound is:



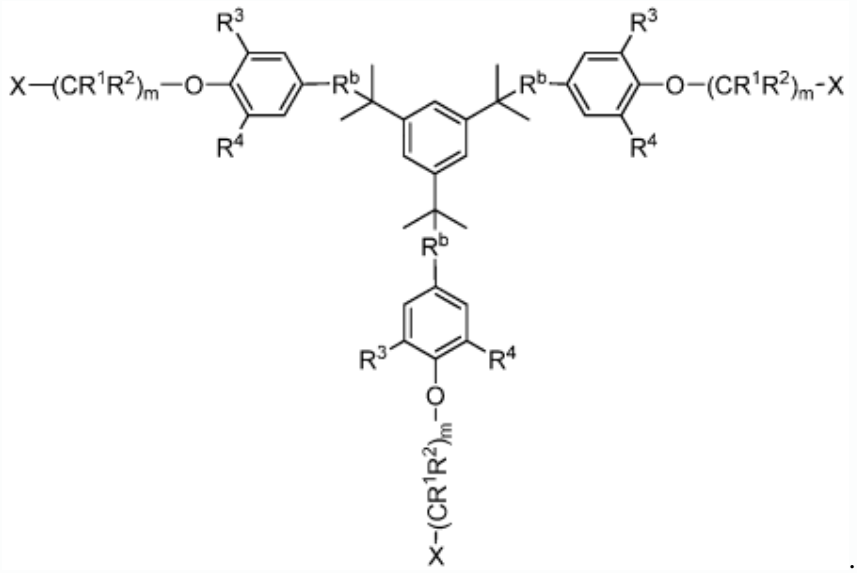
;

or wherein the compound is:



;

or wherein the compound is:



20. The compound of claim 16, wherein:

R^1 and R^2 are both H; or

R^1 and R^2 are independently in each -(CR^1R^2) unit, alkyl of 1 to 6 carbons or hydrogen; or

R^3 and R^4 are identical; or

m is 1-20 and R^3 and R^4 are hydrogen; or

m is 1-20 and R^3 and R^4 are each, independently, alkyl of 1 to 6 carbons or alkoxy of 1 to 6 carbons; or

m is 1 and at least one of R^3 and R^4 is not H; or

m is 1 and R^3 and R^4 are both H; or

m is 0; or

m is 1; or

m is 2; or

m is 3-20; or

m is 1, at least one of R^3 and R^4 is not H, and X is H, alkyl, or alkenyl; or

at least one of R^5-R^7 is tert-butyl; or

at least one of R^5-R^7 is phenyl; or

m is 1, R^3 and R^4 are both H, and X is alkyl, or alkenyl; or

m is 2-20 and X is H, alkyl of 1 to 6 carbons, alkenyl of 2 to 6 carbons, F, Cl, Br, or I; or

m is 2-20 and X is Cl or Br, or m is 3 to 20 and X is OH; or

R^8-R^{11} are each, independently, alkyl of 1 to 6 carbons; or

m is 2; R^1 and R^2 are H; -O-$(CR^1R^2)_m$-X is ortho to R^4, and X and R^4, together, with the atoms to which X and R^4 are attached, form a ring.

21. The compound of claim 16, wherein the compound is:

