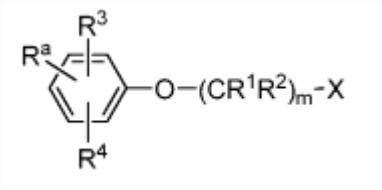
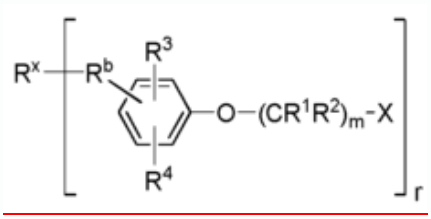
WHAT IS CLAIMED:

1. A method for preparing a compound~~telechelic polymer~~ 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

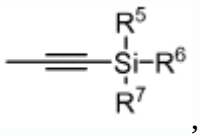
if m is 0,

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



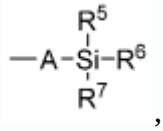
,

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

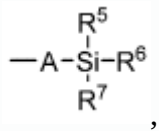
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl,

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 $NR^{10}R^{11}$;

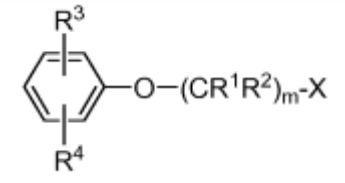
R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, hydroxy, -$NR^{10}R^{11}$, -F, -Cl, -Br, -I, or -At,

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:

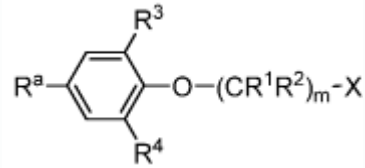
(a) generating a quasiliving carbocationic polyolefin; and

(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:

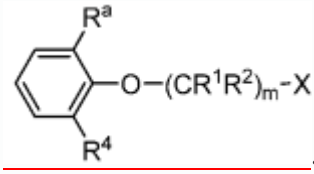


II.

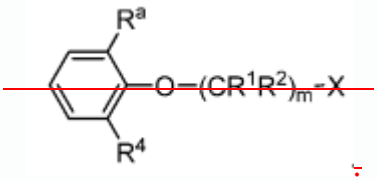
2. The method of claim 1, wherein the compound~~telechelic polymer~~ of formula I is:



or wherein the compound of formula I is:



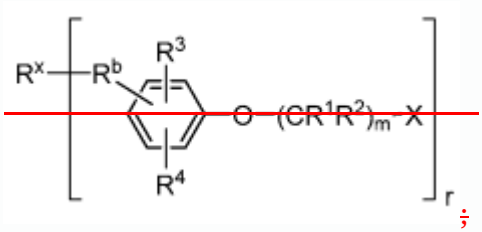
~~3. The method of claim 1, wherein the telechelic polymer of formula I is:~~



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

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

6. The method of claim 5, wherein the telechelic polymer of formula I is:

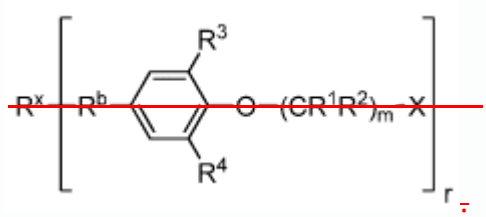


wherein R^b is a polyisobutylene group;

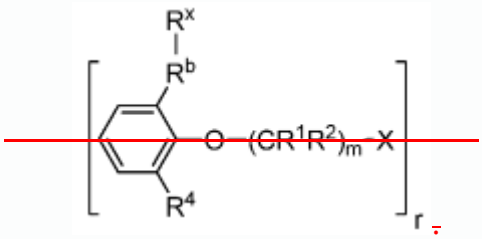
R^x is a polyfunctional carbocationic initiator residue;

and r is an integer from 1 to 4.

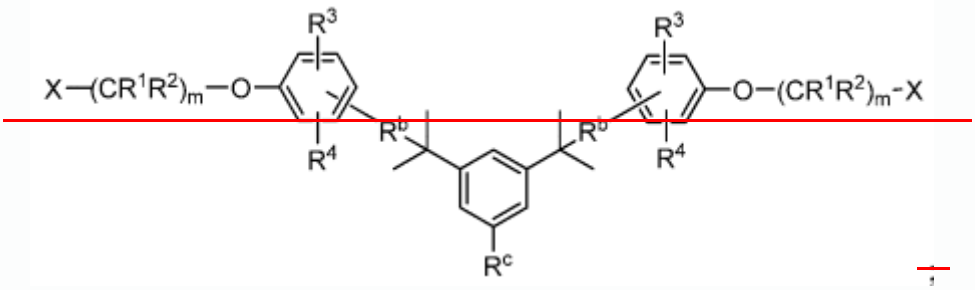
7. The method of claim 6, wherein the telechelic polymer of formula I is:



8. The method of claim 6, wherein the telechelic polymer of formula I is:



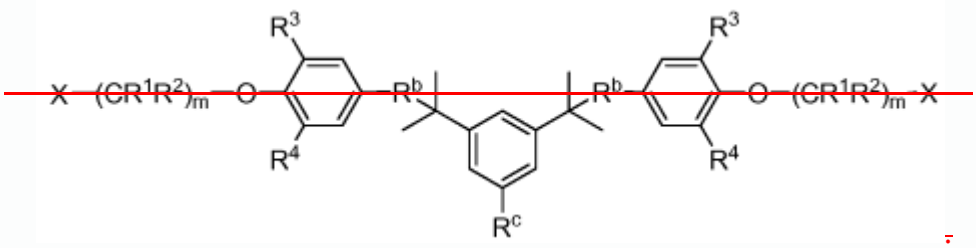
9. The method of claim 6, wherein the telechelic polymer of formula I is:



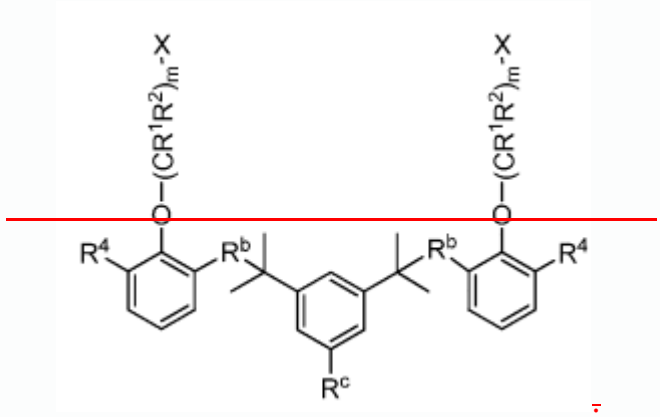
wherein R^c is H or alkyl.

10. The method of claim 9, wherein R is alkyl of 1 to about 6 carbons.

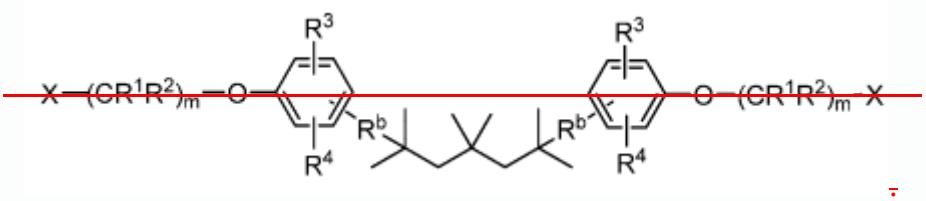
11. The method of claim 9, wherein the telechelic polymer of formula I is:



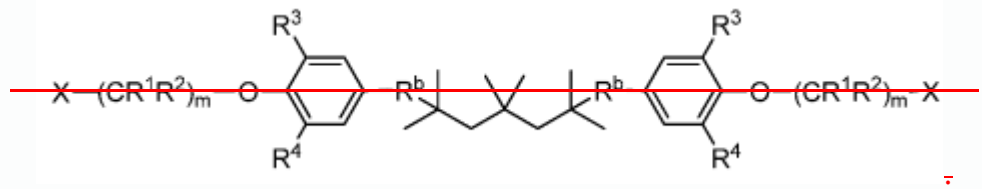
12. The method of claim 9, wherein the telechelic polymer of formula I is:



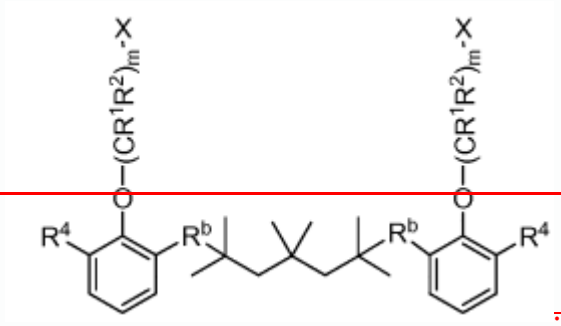
13. The method of claim 5 , wherein the telechelic polymer of formula I is



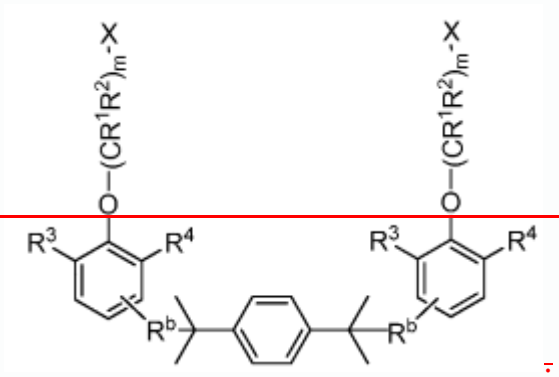
14. The method of claim 13, wherein the telechelic polymer of formula I is



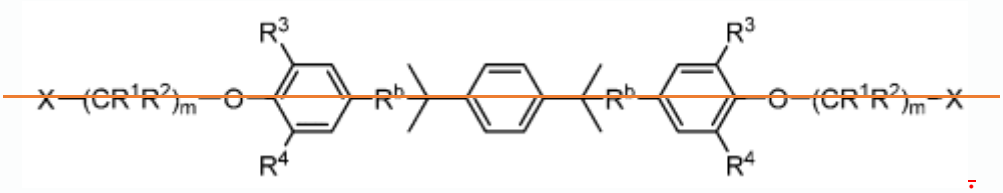
15. The method of claim 13 , wherein the telechelic polymer of formula I is



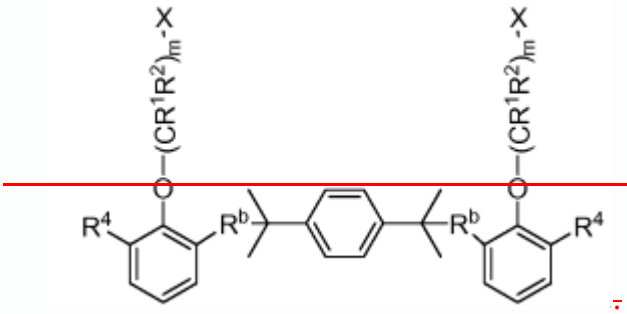
16. The method of claim 13, wherein the telechelic polymer of formula I is



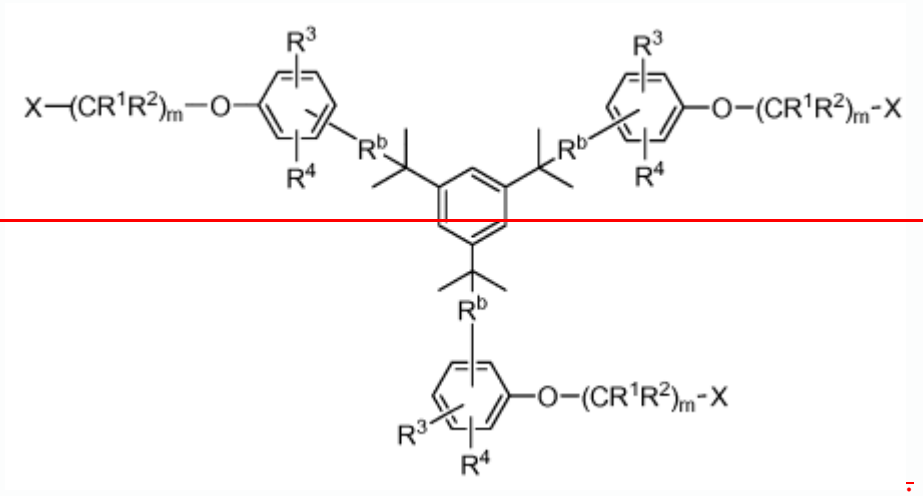
17. The method of claim 13, wherein the telechelic polymer of formula I is



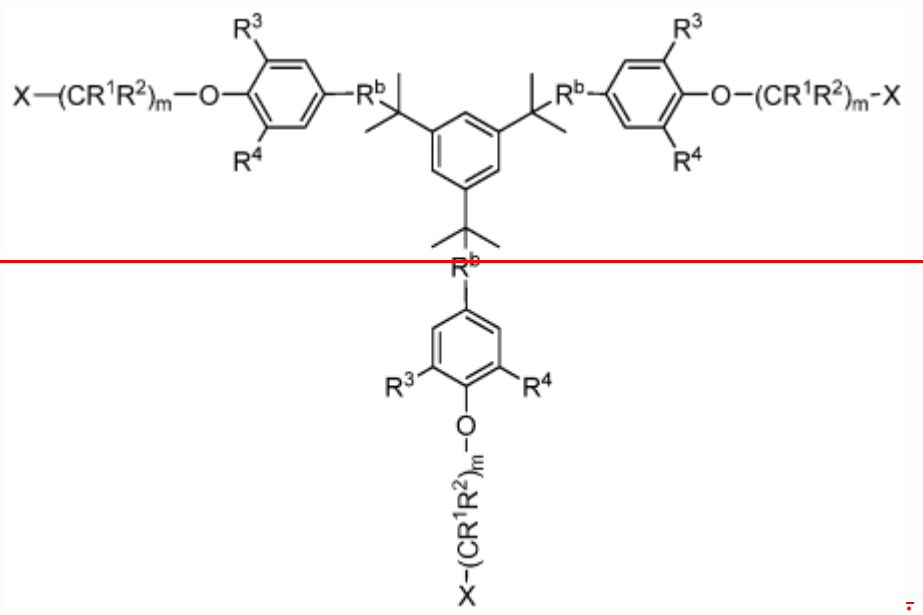
18. The method of claim 13, wherein the telechelic polymer of formula I is



~~19. The method of claim 5, wherein the telechelic polymer of formula I is~~



~~20. The method of claim 19, wherein the telechelic polymer of formula I is~~



~~5~~21. 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

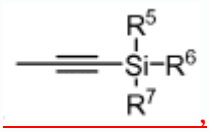
m is 1; or

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

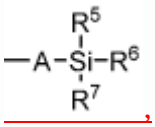
m is 2-20 and X is Cl, or Br; or

m is 3 to 20 and X is OH; or

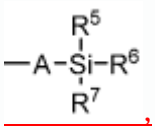
R^8-R^{11} are each, independently, alkyl of 1 to 6 carbons; or

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.

~~22. The method of claim 1, wherein R^1 and R^2 are each, independently in each -(CR^1R^2)- unit, alkyl of 1 to about 6 carbons or hydrogen.~~

~~23. The method of claim 1, wherein R^1 and R^2 are each, independently in each -(CR^1R^2)- unit, methyl or hydrogen.~~

24. The method of claim 1, wherein R^3 and R^4 are identical.

25. The method of claim 1, wherein m is 1-20 and R^3 and R^4 are hydrogen.

26. The method of claim 1 wherein R^3 and R^4 are each, independently, tert-butyl.

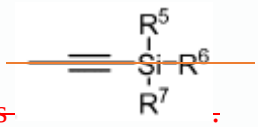
27. The method of claim 1, wherein m is 0.

28. The method of claim 1, wherein m is 1.

29. The method of claim 1, wherein m is 2.

30. The method of claim 1, wherein m is 3-20.

31. The method of claim 1, wherein m is 1 and X is H, alkyl of 1 to about 6 carbons, or alkenyl of 2 to about 6 carbons.

32. The method of claim 1, wherein m is 1 and X is 

.

33. The method of claim 32, wherein at least one of R^5-R^7 is tert-butyl.

34. The method of claim 32, wherein at least one of R^5-R^7 is phenyl.

35. The method of claim 1, wherein m is 2-20 and X is H, alkyl of 1 to about 6 carbons, alkenyl of 2 to about 6 carbons, F, Cl, Br, or I.

36. The method of claim 1, wherein m is 2-20 and X is Cl, or Br.

37. The method of claim 1, wherein m is 3 to 20 and X is OH.

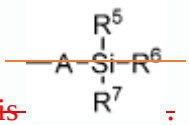
38. The method of claim 1, wherein R^8-R^{11} are each, independently, alkyl of 1 to about 6 carbons.

~~39. The method of claim 1, wherein m is 2;~~

~~R^1 and R^2 are H;~~

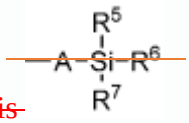
~~$-O-(CR^1R^2)_m-X$ is ortho to R^4; and~~

~~X and R^4, together, with the atoms to which X and R^4 are attached, form a ring.~~

~~40. The method of claim 1, wherein m is 2 and X is~~  ~~.~~

~~41. The method of claim 40, wherein at least one of R^5-R^7 is tert-butyl~~

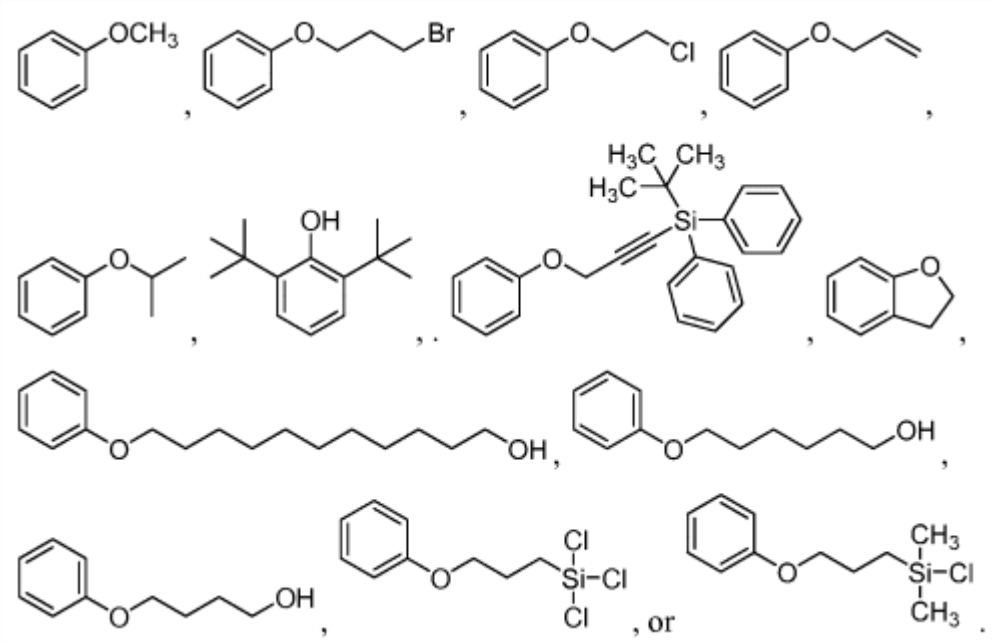
~~42. The method of claim 40, wherein at least one of R^5-R^7 is phenyl.~~

~~43. The method of claim 1, wherein m is 3-20 and X is~~ 

~~44. The method of claim 43, wherein at least one of R^5-R^7 is tert-butyl.~~

~~45. The method of claim 43, wherein at least one of R^5-R^7 is phenyl.~~

6~~46~~. The method of claim 1, wherein the compound of formula II is



747. 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.

848. The method of claim 747, 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).

~~49. The method of claim 47, wherein the initiator is 2-chloro-2,4,4-trimethylpentane.~~

~~50. The method of claim 47, wherein the initiator is bifunctional.~~

~~51. The method of claim 47, wherein the initiator is 5-tert-butyl-l,3-bis(l-chloro-1-methylethyl)benzene.~~

~~52. The method of claim 47, wherein the initiator is multifunctional.~~

~~53. The method of claim 47, wherein the initiator is l,3,5-tri(2-chloro-2-propyl)benzene or l,3,5-tri(2-methoxy-2-propyl)benzene.~~

954. The method of claim 747, wherein the monomer is isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, or 4-methyl-l-pentene, or wherein the monomer is isobutylene.

~~55. The method of claim 47, wherein the monomer is isobutylene.~~

1056. The method of claim 747, 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.

~~57. The method of claim 47, wherein the common ion salt precursor is tetrabutylammonium chloride or tetrabutylammonium iodide.~~

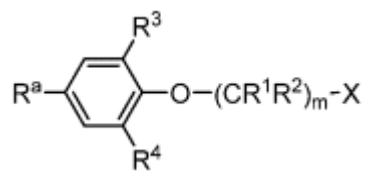
~~58. The method of claim 47, wherein the Lewis acid is a titanium tetrahalide, a boron trihalide, aluminum trichloride, tin tetrachloride, zinc chloride, or ethyl aluminum dichloride, or mixtures thereof.~~

~~59. The method of claim 47, wherein the Lewis acid is titanium tetrachloride.~~

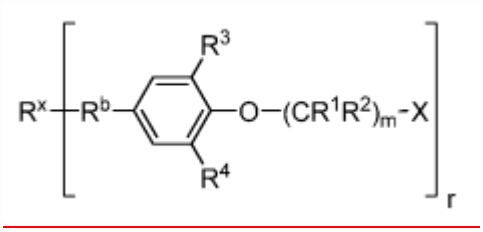
~~60. The method of claim 47, wherein a mixture of Lewis acids is used.~~

11~~61~~. The method of claim 1, wherein a diluent is used.

12~~62~~. The method of claim 1, wherein

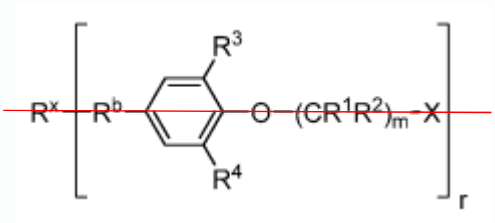


is the major isomer product, or wherein



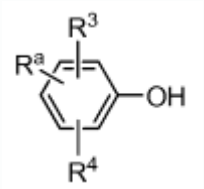
is the major isomer product.

~~63. The method of claim 6, wherein~~



~~is the major isomer product.~~

13~~64~~. 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~~65~~. The method of claim 13~~64~~, 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.

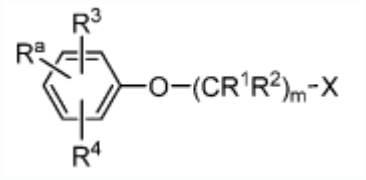
~~66. The method of claim 64, wherein the acid is BBr_3, BCl_3, $AlCl_3$, $AlBr_3$, $TiCl_4$, or $TiBr_4$.~~

~~67. The method of claim 64, wherein the acid is BBr_3.~~

1568. The method of claim 1465, 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.

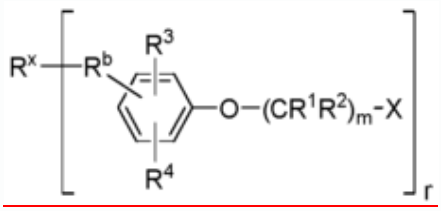
~~69. The method of claim 68, wherein the protic acid is H_2SO_4, HBr, HCl, trifluoroacetic acid, para-toluenesulfonic acid, or methanesulfonic acid.~~

1670. 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

~~wherein~~ m is an integer from 1 to 20; wherein

if m is 0,

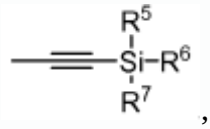
then R^3 and R^4 are each, independently, alkyl, and

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



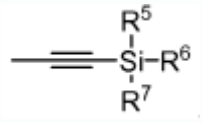
,

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



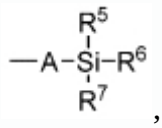
,

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

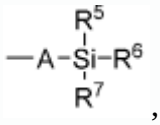
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl,

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 $-NR^{10}R^{11}$;

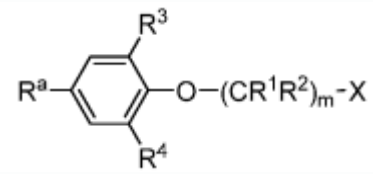
R^5-R^7 are each, independently, alkyl, alkenyl, alkynyl, alkaryl, aralkyl, aryl, heteroaryl, alkoxy, or hydroxy,

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

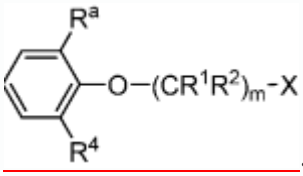
R^9-R^{11} are each, independently, H, alkyl, alkenyl, alkynyl, alkaryl, aryl, or heteroaryl.

1771. The compound of claim 1670, wherein the polyolefin group is a polyisobutyl group.

1872. The compound of claim 1670, wherein the compound:

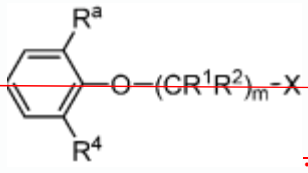


or wherein the compound is



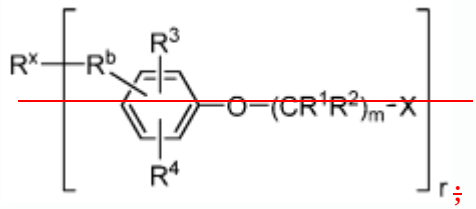
.

~~73. The compound of claim 70, wherein the compound is:~~



~~.~~

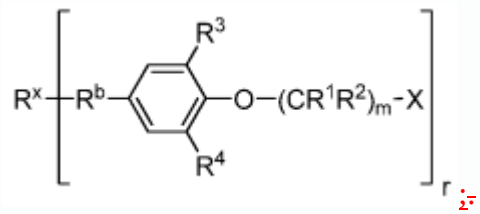
~~74. The compound of claim 70, wherein the compound is:~~



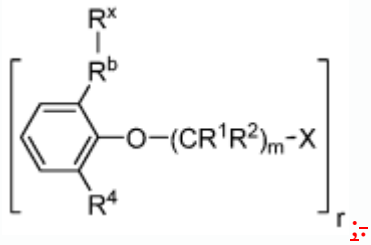
~~;~~

~~wherein R^b is a polyisobutylene group;~~
~~R^x is a polyfunctional carbocationic initiator residue;~~
~~and r is an integer from 1 to 4.~~

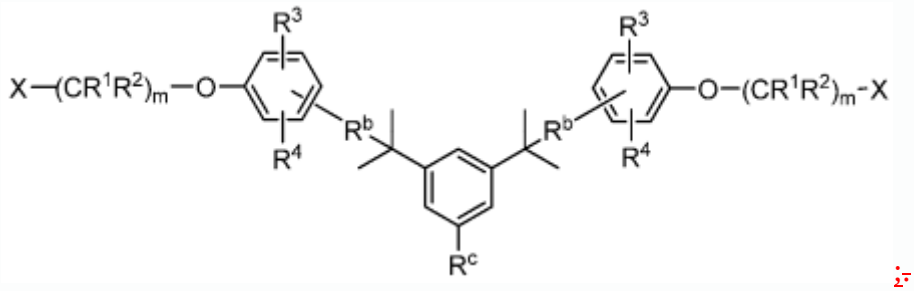
1975. The method of claim 4 or the compound of claim 1674, wherein the compound is:



76. The compound of claim 74, or wherein the compound is:

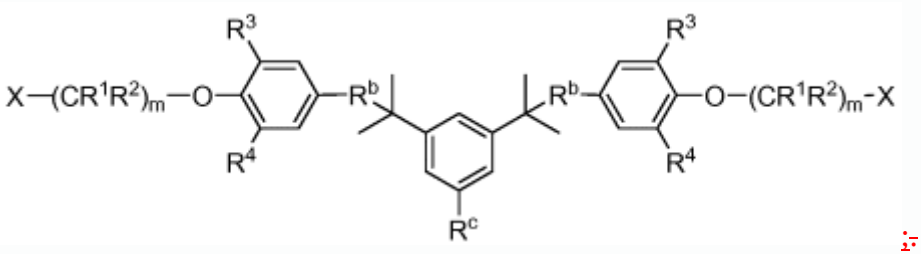


77. The compound of claim 74,or wherein the compound is:

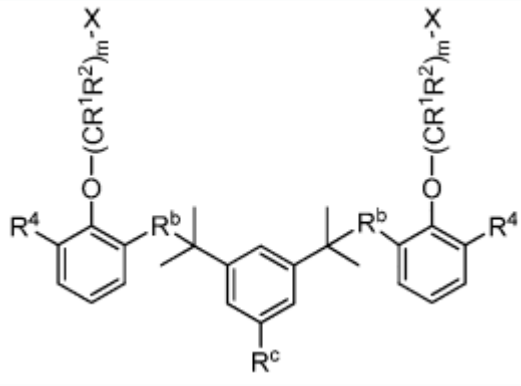


wherein R^c is H or alkyl, optionally wherein R^c is alkyl of 1 to 6 carbons; or.

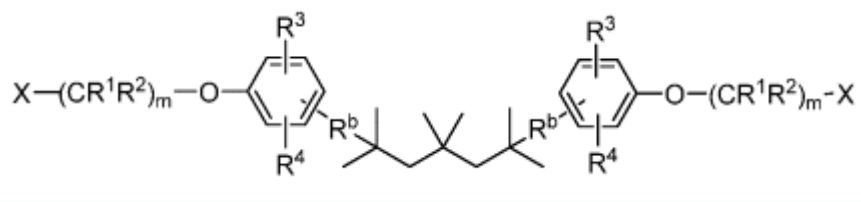
78. The compound of claim 77, wherein the compound is:



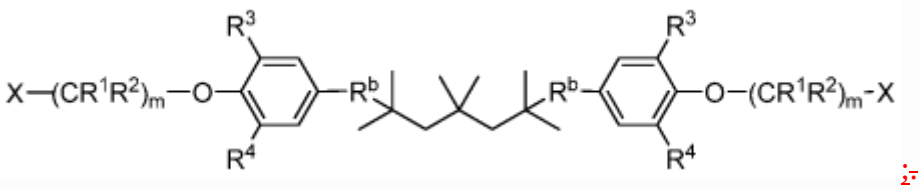
~~79. The compound of claim 77,~~or wherein the compound is:



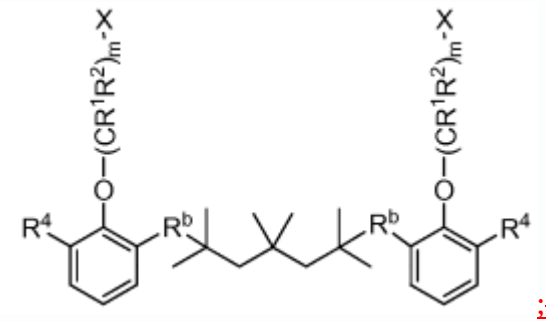
~~80. The compound of claim 74,~~or wherein the compound is:



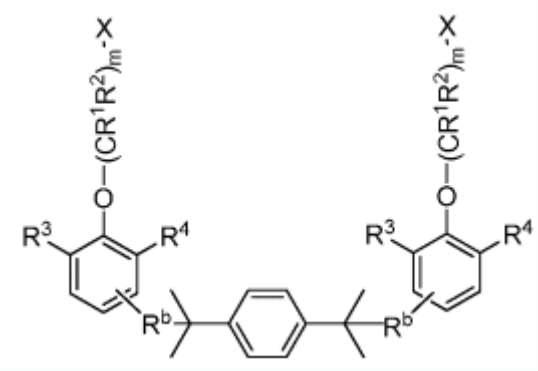
~~81. The compound of claim 80,~~or wherein the compound is:



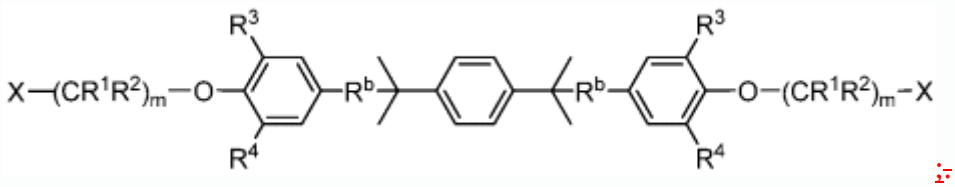
~~82. The compound of claim 80,~~or wherein the compound is:



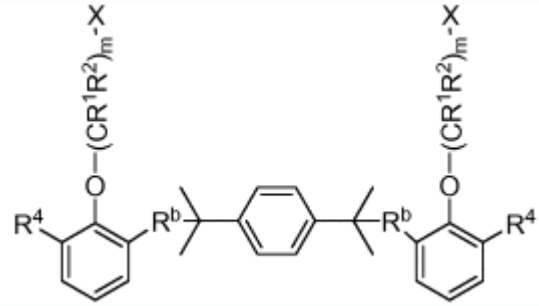
~~83. The compound of claim 74,~~or wherein the compound is:



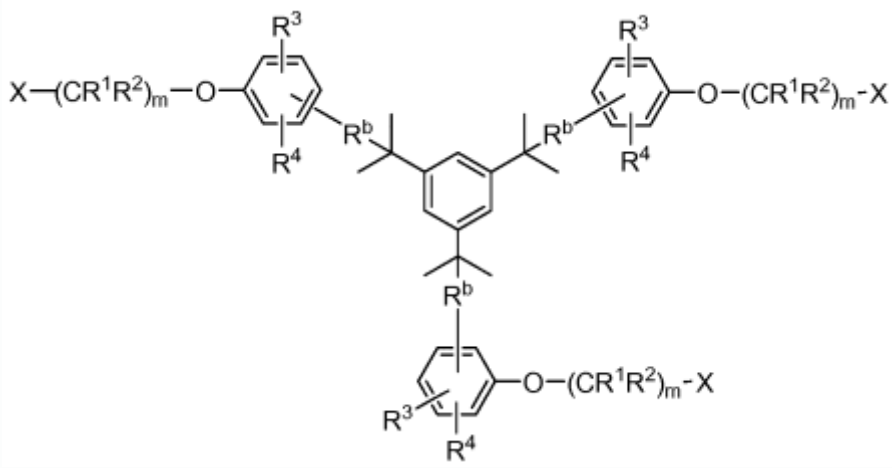
~~84. The compound of claim 83,~~or wherein the compound is:



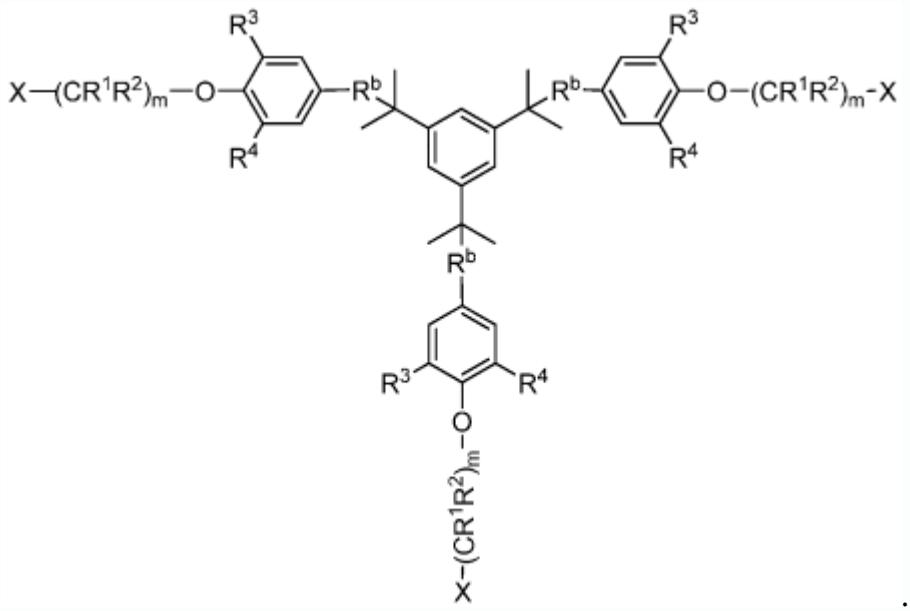
~~85. The compound of claim 83,~~or wherein the compound is:



~~86. The compound of claim 74,~~or wherein the compound is:



~~87. The compound of claim 86,~~or wherein the compound is:



.

~~88. The compound of claim 77, wherein R^e is alkyl of 1 to about 6 carbons.~~

20~~89~~. The compound of claim 16~~70~~, wherein:

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

~~90. The compound of claim 70, wherein~~ R^1 and R^2 are independently in each -(CR^1R^2) unit, alkyl of 1 to ~~about~~ 6 carbons or hydrogen~~.~~; or

~~91. The compound of claim 70, wherein~~ R^3 and R^4 are identical~~.~~; or

~~92. The compound of claim 70, wherein~~ m is 1-20 and R^3 and R^4 are hydrogen~~.~~; or

~~93. The compound of claim 70, wherein~~ m is 1-20 and R^3 and R^4 are each, independently, alkyl of 1 to ~~about~~ 6 carbons or alkoxy of 1 to ~~about~~ 6 carbons; or.

~~94. The compound of claim 70, wherein~~ m is 1 and at least one of R^3 and R^4 is not H~~.~~; or

~~95. The compound of claim 70, wherein~~ m is 1 and R^3 and R^4 are both H~~.~~; or

~~96. The compound of claim 70, wherein~~ m is 0~~.~~; or

~~97. The compound of claim 70, wherein~~ m is 1~~.~~; or

~~98. The compound of claim 70, wherein~~ m is 2~~.~~; or

~~99. The compound of claim 70, wherein~~ m is 3-20~~.~~; or

~~100. The compound of claim 70, wherein~~ m is 1, at least one of R^3 and R^4 is not H, and X is H, alkyl, or alkenyl~~.~~; or

~~101. The compound of claim 70, wherein~~ at least one of R^5-R^7 is tert-butyl~~.~~; or

~~102. The compound of claim 70, wherein~~ at least one of R^5-R^7 is phenyl~~.~~; or

~~103. The compound of claim 70, wherein~~ m is 1, R^3 and R^4 are both H, and X is alkyl, or alkenyl~~.~~; or

~~104. The compound of claim 70, wherein~~ m is 2-20 and X is H, alkyl of 1 to ~~about~~ 6 carbons, alkenyl of 2 to ~~about~~ 6 carbons, F, Cl, Br, or I~~.~~; or

~~105. The compound of claim 70, wherein~~ m is 2-20 and X is Cl or Br~~.~~, or

~~106. The compound of claim 70, wherein~~ m is 3 to 20 and X is OH~~.~~; or

~~107. The compound of claim 70, wherein~~ R^8-R^{11} are each, independently, alkyl of 1 to ~~about~~ 6 carbons~~.~~; or

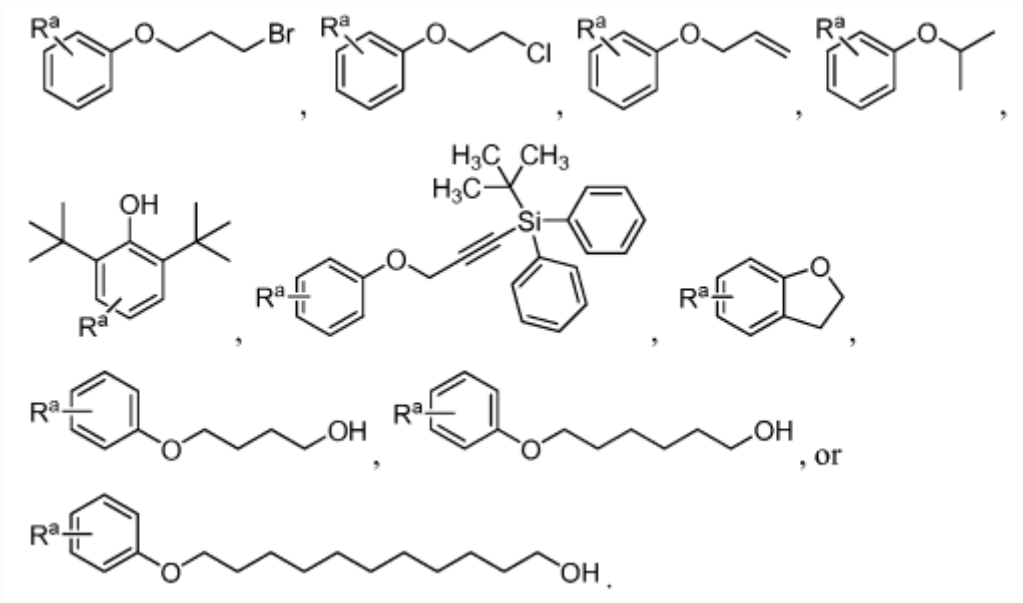
~~108. The compound of claim 70, wherein~~ m is 2;

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~~09~~. The compound of claim 16~~70~~, wherein the compound is:



~~110. The compound of claim 70, wherein the compound is a para isomer.~~

~~111. The compound of claim 70, wherein the compound is between about 1.0×10^{3} g/mol to about 1.0×10^{5} g/mol.The telechelic polymer prepared by the method of claim 1.~~