(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 September 2012 (27.09.2012)

(10) International Publication Number
WO 2012/129090 A1

(51) International Patent Classification:
C08G 75/12 (2006.01) ***C09D 181/02*** (2006.01)

(21) International Application Number:
PCT/US2012/029436

(22) International Filing Date:
16 March 2012 (16.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/050,988 18 March 2011 (18.03.2011) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- — *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- — *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- — *with international search report (Art. 21(3))*

(54) Title: TERMINAL-MODIFIED DIFUNCTIONAL SULFUR-CONTAINING POLYMERS, COMPOSITIONS THEREOF AND METHODS OF USE

(57) Abstract: Disclosed are terminal-modified difunctional sulfur-containing polymers that are the reaction products of a sulfur-containing diol, an aldehyde or a ketone, and a compound containing a functional group. Compositions comprising the terminal-modified difunctional sulfur-containing polymers useful as sealants are also disclosed.

TERMINAL-MODIFIED DIFUNCTIONAL SULFUR-CONTAINING POLYMERS, COMPOSITIONS THEREOF AND METHODS OF USE

FIELD

[001] The present disclosure relates to terminal-modified difunctional sulfur-containing polymers, compositions comprising terminal-modified difunctional sulfur-containing polymers, and methods of using terminal-modified difunctional sulfur-containing polymers.

BACKGROUND

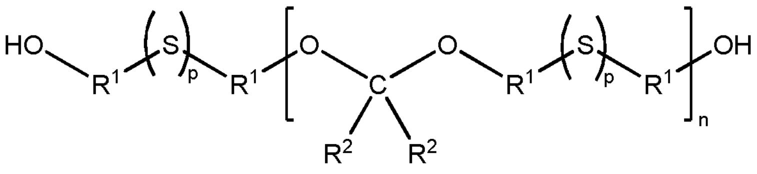
[002] Thiol-terminated sulfur-containing polymers are known to be well-suited for use in various applications such as aerospace sealant compositions, due, in large part, to their fuel-resistance. Other desirable properties for aerospace sealant compositions include low temperature flexibility, short curing time (the time required to reach a predetermined strength), and elevated-temperature resistance, among others. Sealant compositions exhibiting at least some of these characteristics and containing thiol-terminated sulfur-containing polymers are described, for example, in U.S. Patent Nos. 2,466,963, 4,366,307, 4,609,762, 5,225,472, 5,912,319, 5,959,071, 6,172,179, 6,232,401, 6,372,849, and 6,509,418. Polythioethers that are liquid at room temperature and pressure and that have excellent low temperature flexibility and fuel resistance, such as those disclosed in U.S. Patent No. 6,172,179, are also useful in aerospace sealant applications. For example, difunctional polythioethers having terminal hydroxyl groups prepared by reacting a hydroxyl compound with an aldehyde are described, in GB 850,178, U.S. Patent Nos. 3,290,382, 3,959,227, and 3,997,614. Difunctional polythioethers terminated or capped with isocyanates are also known as disclosed, for example, in GB 850,178, and in U.S. Patent Nos. 3,290,382, 3,959,227, and 3,997,614.

[003] Polysulfides are also used in aerospace sealant applications where they provide high tensile strength, high shear strength, high-temperature thermal resistance, and fuel resistance, as disclosed, for example in U.S. Patent No. 7,638,162 and U.S. Publication No. 2005/0245695.

SUMMARY

[004] Sulfur-containing polymers terminated with other functional groups can enable the use of alternative curing chemistries and can provide sealants having enhanced properties suitable for aerospace sealant applications.

[005] In a first aspect of the present disclosure, terminal-modified sulfur-containing polymers are provided comprising the reaction products of reactants comprising: (a) a sulfur-containing polymer of Formula (I):



(I)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (b) a compound comprising a terminal group selected from a vinyl group, a silyl group, and an epoxy group; and a group selected from a group that is reactive with the terminal hydroxyl groups of the polymer of Formula (I).

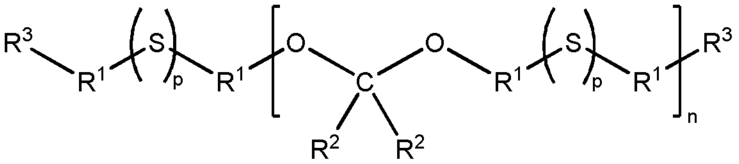
[006] In a second aspect of the present disclosure, terminal-modified sulfur-containing polymers are provided comprising the reaction products of reactants comprising: (a) and (b), wherein (a) comprises the reaction products of reactants comprising: (i) and (ii), wherein (i) comprises a sulfur-containing polymer of Formula (I), wherein n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (ii) comprises a first compound selected from a diisocyanate, an ethylenically unsaturated isocyanate, and a tosylate; and (b) comprises a second compound comprising a terminal group selected from a vinyl group, a silyl group, and an epoxy group; and a group selected

from a group that is reactive with an isocyanate group, an ethylenically unsaturated group, and a tosylate.

[007] In a third aspect of the present disclosure, amine-terminated sulfur-containing polymers are provided comprising the reaction products of reactants comprising: (a) and (b), wherein (a) comprises the reaction products of reactants comprising (i) and (ii), wherein (i) comprises a sulfur-containing polymer of Formula (I), wherein n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (ii) comprises a first compound selected from a diisocyanate, an activated ethylenically unsaturated isocyanate, and a tosylate; and (b) comprises a second compound comprising an amine group and a group selected from a group that is reactive with an isocyanate group, an ethylenically unsaturated group, and a tosylate.

[008] In a fourth aspect of the present disclosure, thiol-terminated sulfur-containing polymers are provided comprising the reaction products of reactants comprising: (a) and (b), wherein (a) comprises the reaction products of reactants comprising (i) and (ii), wherein (i) comprises a sulfur-containing polymer of Formula (I), wherein n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (ii) comprises a first compound selected from a diisocyanate, thiourea, an ethylenically unsaturated isocyanate, and a tosylate; and (b) comprises a mercaptoalkanol when (ii) comprises a diisocyanate; a metal hydrosulfide when (ii) comprises thiourea; a dithiol when (ii) comprises an ethylenically unsaturated isocyanate; and a metal hydrosulfide when (ii) comprises a tosylate.

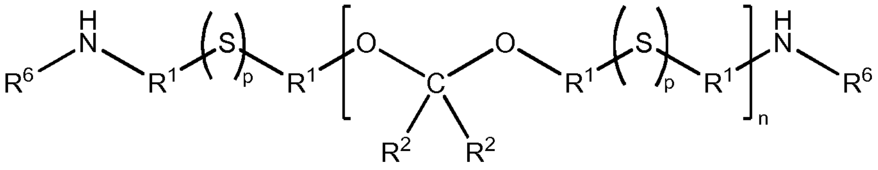
[009] In a fifth aspect of the present disclosure, terminal-modified sulfur-containing polymers of Formula (II) are provided:



(II)

wherein n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and each R^3 is $-OR^{3'}$ wherein $R^{3'}$ is independently selected from a vinyl-terminated group, a silyl-terminated group, an amine-terminated group, an epoxy-terminated group, and a thiol-terminated group.

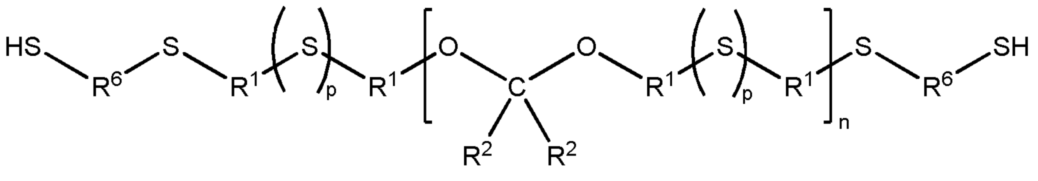
[010] In a sixth aspect of the present disclosure, amine-terminated sulfur-containing polymers of Formula (III) are provided:



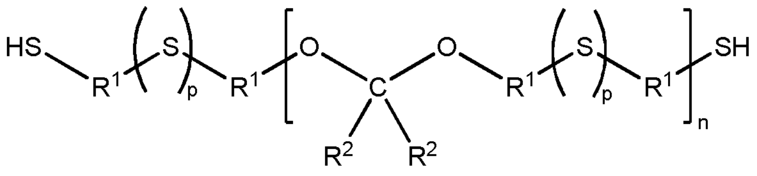
(III)

wherein n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{2-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and each R^6 is independently selected from hydrogen, C_{5-6} cycloalkyl, phenyl, and C_{1-6} alkyl.

[011] In a seventh aspect of the present disclosure, thiol-terminated sulfur-containing polymers of Formula (IVa) and Formula (IVb) are provided:



(IVa)



(IVb)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and each R^6 is independently selected from C_{1-6} alkanediyl and C_{5-12} heteroalkanediyl.

[012] In an eighth aspect of the present disclosure, compositions are provided comprising a terminal-modified sulfur-containing polymer provided by the present disclosure and a curing agent that is reactive with the terminal-modified sulfur-containing polymer.

[013] In a ninth aspect of the present disclosure, apertures are provided that are sealed with a sealant comprising a composition comprising a terminal-modified sulfur-containing polymer provided by the present disclosure and a curing agent that is reactive with the terminal-modified sulfur-containing polymer.

[014] The present disclosure is also directed to methods for making terminal-modified sulfur-containing polymers and compositions thereof, such as sealant compositions, including aerospace sealant compositions, comprising terminal-modified sulfur-containing polymers provided by the present disclosure.

DETAILED DESCRIPTION

Definitions

[015] A dash ("–") that is not between two letters or symbols is used to indicate a point of bonding for a substituent or between two atoms. For example, –$CONH_2$ is bonded to another moiety through the carbon atom.

[016] "Activated ethylenically unsaturated isocyanate" refers to a compound comprising an ethylenically unsaturated group and an isocyanate group in which the double bond is electron deficient such that it is activated toward Michael addition, *i.e.*, the double bond is a Michael acceptor.

[017] "Aldehyde" refers to a compound of the formula CH(O)R where R is hydrogen or a hydrocarbon group such as an alkyl group, as defined herein. In certain embodiments, the aldehyde is C_{1-10} aldehyde, C_{1-6} aldehyde, C_{1-4} aldehyde, C_{1-3} aldehyde, and in certain embodiments, C_{1-2} aldehyde. In certain embodiments, the aldehyde is formaldehyde. In certain embodiments of the aldehyde, R is selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl.

[018] "Alkanediyl" refers to a diradical of a saturated, branched or straight-chain, acyclic hydrocarbon group, having, for example, from 1 to 18 carbon atoms (C_{1-18}), from 1-14 carbon atoms (C_{1-14}), from 1-6 carbon atoms (C_{1-6}), from 1 to 4 carbon atoms (C_{1-4}), or from 1 to 3 hydrocarbon atoms (C_{1-3}). In certain embodiments, the alkanediyl is C_{2-14} alkanediyl, C_{2-10} alkanediyl, C_{2-8} alkanediyl, C_{2-6} alkanediyl, C_{2-4} alkanediyl, and in certain embodiments, C_{2-3} alkanediyl. Examples of alkanediyl groups include methane-diyl (–CH_2–), ethane-1,2-diyl (–CH_2CH_2–), propane-1,3-diyl and iso-propane-1,2-diyl (*e.g.*, –$CH_2CH_2CH_2$– and –$CH(CH_3)CH_2$–), butane-1,4-diyl (–$CH_2CH_2CH_2CH_2$–), pentane-1,5-diyl (–$CH_2CH_2CH_2CH_2CH_2$–), hexane-1,6-diyl (–$CH_2CH_2CH_2CH_2CH_2CH_2$–), heptane-1,7-diyl, octane-1,8-diyl, nonane-1,9-diyl, decane-1,10-diyl, dodecane-1,12-diyl, and the like.

[019] "Alkanedithiol" refers to an alkane group in which two of the hydrogen atoms are replaced with a thiol group, –SH. In certain embodiments, the alkanedithiol is C_{2-12} alkanedithiol, C_{2-10} alkanedithiol, C_{2-8} alkanedithiol, C_{2-6} alkanedithiol, and in certain embodiments, C_{2-3} alkanedithiol.

[020] "Alkanearene" refers to a hydrocarbon group having one or more aryl and/or arenediyl groups and one or more alkyl and/or alkanediyl groups, where aryl, arenediyl, alkyl, and alkanediyl are defined here. In certain embodiments, each aryl and/or arenediyl group(s) is C_{6-12}, C_{6-10}, and in certain embodiments, phenyl or benzenediyl. In certain embodiments, each alkyl and/or alkanediyl group(s) is C_{1-6}, C_{1-4}, C_{1-3}, and in certain embodiments, methyl, methanediyl, ethyl, or ethane-1,2-diyl. In certain embodiments, the alkanearene group is C_{4-18} alkanearene, C_{4-16} alkanearene, C_{4-12} alkanearene, C_{4-8} alkanearene, C_{6-12} alkanearene, C_{6-10} alkanearene, and in certain embodiments, C_{6-9} alkanearene. Examples of alkanearene groups include diphenyl methane.

[021] "Alkanearenediyl" refers to a diradical of an alkanearene group. In certain embodiments, the alkanearenediyl group is C_{4-18} alkanearenediyl, C_{4-16} alkanearenediyl, C_{4-12} alkanearenediyl, C_{4-8} alkanearenediyl, C_{6-12} alkanearenediyl, C_{6-10} alkanearenediyl, and in certain embodiments, C_{6-9} alkanearenediyl. Examples of alkanearenediyl groups include diphenyl methane-4,4'-diyl.

[022] "Alkanecycloalkane" refers to a saturated hydrocarbon group having one or more cycloalkyl and/or cycloalkanediyl groups and one or more alkyl and/or alkanediyl groups, where cycloalkyl, cycloalkanediyl, alkyl, and alkanediyl are defined herein. In certain embodiments, each cycloalkyl and/or cycloalkanediyl group(s) is C_{3-6}, C_{5-6}, and in certain embodiments, cyclohexyl or cyclohexanediyl. In certain embodiments, each alkyl and/or alkanediyl group(s) is C_{1-6}, C_{1-4}, C_{1-3}, and in certain embodiments, methyl, methanediyl, ethyl, or ethane-1,2-diyl. In certain embodiments, the alkanecycloalkane group is C_{4-18} alkanecycloalkane, C_{4-16} alkanecycloalkane, C_{4-12} alkanecycloalkane, C_{4-8} alkanecycloalkane, C_{6-12} alkanecycloalkane, C_{6-10} alkanecycloalkane, and in certain embodiments, C_{6-9} alkanecycloalkane. Examples of alkanecycloalkane groups include 1,1,3,3-tetramethylcyclohexane and cyclohexylmethane.

[023] "Alkanecycloalkanediyl" refers to a diradical of an alkanecycloalkane group. In certain embodiments, the alkanecycloalkanediyl group is C_{4-18} alkanecycloalkanediyl, C_{4-16} alkanecycloalkanediyl, C_{4-12} alkanecycloalkanediyl, C_{4-8} alkanecycloalkanediyl, C_{6-12} alkanecycloalkanediyl, C_{6-10} alkanecycloalkanediyl, and in certain embodiments, C_{6-9} alkanecycloalkanediyl. Examples of

alkanecycloalkanediyl groups include 1,1,3,3-tetramethylcyclohexane-1,5-diyl and cyclohexylmethane-4,4'-diyl.

[024] "Alkoxy" refers to an –OR group where R is alkyl as defined herein. Examples of alkoxy groups include methoxy, ethoxy, n-propoxy, isopropoxy, and n-butoxy. In certain embodiments, the alkoxy group is C_{1-8} alkoxy, C_{1-6} alkoxy, C_{1-4} alkoxy, and in certain embodiments, C_{1-3} alkoxy.

[025] "Alkyl" refers to a monoradical of a saturated, branched or straight-chain, acyclic hydrocarbon group having, for example, from 1 to 20 carbon atoms, from 1 to 10 carbon atoms, from 1 to 6 carbon atoms, from 1 to 4 carbon atoms, or from 1 to 3 carbon atoms. In certain embodiments, the alkyl group is C_{2-6} alkyl, C_{2-4} alkyl, and in certain embodiments, C_{2-3} alkyl. Examples of alkyl groups include methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-hexyl, n-decyl, tetradecyl, and the like. In certain embodiments, the alkyl group is C_{2-6} alkyl, C_{2-4} alkyl, and in certain embodiments, C_{2-3} alkyl.

[026] "Aminoalkyl" refers to an alkyl group as defined herein, in which one of the hydrogen atoms of the alkyl group is replaced with an amino group, $-NH_2$. In certain embodiments, the aminoalkyl group is C_{1-10} aminoalkyl, C_{1-6} aminoalkyl, C_{1-4} aminoalkyl, C_{1-3} aminoalkyl, and in certain embodiments, C_{1-2} aminoalkyl.

[027] "Arenediyl" refers to diradical monocyclic or polycyclic aromatic group. Examples of arenediyl groups include benzene-diyl and naphthalene-diyl. In certain embodiments, the arenediyl group is C_{6-12} arenediyl, C_{6-10} arenediyl, C_{6-9} arenediyl, and in certain embodiments, benzene-diyl.

[028] "Aryl" refers to a monovalent aromatic hydrocarbon radical derived by the removal of one hydrogen atom from a single carbon atom of a parent aromatic ring system. Aryl encompasses 5- and 6-membered carbocyclic aromatic rings, for example, benzene; bicyclic ring systems wherein at least one ring is carbocyclic and aromatic, for example, naphthalene, indane, and tetralin; and tricyclic ring systems wherein at least one ring is carbocyclic and aromatic, for example, fluorene. Aryl encompasses multiple ring systems having at least one carbocyclic aromatic ring fused to at least one carbocyclic aromatic ring, cycloalkyl ring, or heterocycloalkyl ring. For example, aryl includes 5- and 6-membered carbocyclic aromatic rings fused to a 5- to 7-membered heterocycloalkyl ring containing one or more heteroatoms

chosen from N, O, and S. For such fused, bicyclic ring systems wherein only one of the rings is a carbocyclic aromatic ring, the point of attachment may be at the carbocyclic aromatic ring or the heterocycloalkyl ring. Examples of aryl groups include, but are not limited to, groups derived from aceanthrylene, acenaphthylene, acephenanthrylene, anthracene, azulene, benzene, chrysene, coronene, fluoranthene, fluorene, hexacene, hexaphene, hexalene, as-indacene, s-indacene, indane, indene, naphthalene, octacene, octaphene, octalene, ovalene, penta-2,4-diene, pentacene, pentalene, pentaphene, perylene, phenalene, phenanthrene, picene, pleiadene, pyrene, pyranthrene, rubicene, triphenylene, trinaphthalene, and the like. In certain embodiments, the aryl group can have from 6 to 20 carbon atoms, and in certain embodiments, from 6 to 12 carbon atoms. Aryl, however, does not encompass or overlap in any way with heteroaryl, separately defined herein. Hence, a multiple ring system in which one or more carbocyclic aromatic rings is fused to a heterocycloalkyl aromatic ring, is heteroaryl, not aryl, as defined herein. In certain embodiments, an aryl group is phenyl.

[029] “Arylalkyl” refers to an alkyl group in which one of the hydrogen atoms is replaced with an aryl group. In certain embodiments of an arylalkyl group, a hydrogen atom on the terminal carbon atom of an alkyl group is replaced with an aryl group. In certain embodiments of arylalkyl, the aryl group is a C_{6-12} aryl group, in certain embodiments a C_{6-10} aryl group, and in certain embodiments, a phenyl or naphthyl group. In certain embodiments, the alkanediyl portion of an arylalkyl group may be, for example, C_{1-10} alkanediyl, C_{1-6} alkanediyl, C_{1-4} alkanediyl, C_{1-3} alkanediyl, propane-1,3-diyl, ethane-1,2-diyl, or methane-diyl. In certain embodiments, the arylalkyl group is C_{7-18} arylalkyl, C_{7-16} arylalkyl, C_{7-12} arylalkyl, C_{7-10} arylalkyl, or C_{7-9} arylalkyl. For example, C_{7-9} arylalkyl can include a C_{1-3} alkyl group bonded to a phenyl group.

[030] “Cycloalkanediyl” refers to a diradical saturated monocyclic or polycyclic hydrocarbon group. In certain embodiments, the cycloalkanediyl group is C_{3-12} cycloalkanediyl, C_{3-8} cycloalkanediyl, C_{3-6} cycloalkanediyl, and in certain embodiments, C_{5-6} cycloalkanediyl. Examples of cycloalkanediyl groups include cyclohexane-1,4-diyl, cyclohexane-1,3-diyl, and cyclohexane-1,2-diyl.

[031] "Cycloalkyl" refers to a saturated monocyclic or polycyclic hydrocarbon monoradical group. In certain embodiments, the cycloalkyl group is C_{3-12} cycloalkyl, C_{3-8} cycloalkyl, C_{3-6} cycloalkyl, and in certain embodiments, C_{5-6} cycloalkyl.

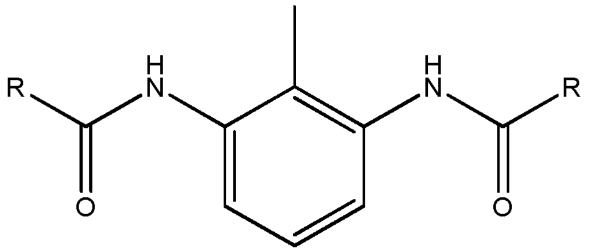
[032] "Cycloalkylalkyl" refers to an alkyl group in which one of the hydrogen atoms is replaced with a cycloalkyl group. In certain embodiments of the cycloalkylalkyl group, a hydrogen atom on the terminal carbon atom of an alkyl group is replaced with a cycloalkyl group. In certain embodiments of cycloalkylalkyl, the cycloalkyl group is a C_{3-6} cycloalkyl group, in certain embodiments a C_{5-6} cycloalkyl group, and in certain embodiments, a cyclopropyl, a cyclobutyl, a cyclopentyl, or a cyclohexyl group. In certain embodiments, the alkanediyl portion of a cycloalkylalkyl group may be, for example, C_{1-10} alkanediyl, C_{1-6} alkanediyl, C_{1-4} alkanediyl, C_{1-3} alkanediyl, propane-1,3-diyl, ethane-1,2-diyl, or methane-diyl. In certain embodiments, the cycloalkylalkyl group is C_{4-16} cycloalkylalkyl, C_{4-12} cycloalkylalkyl, C_{4-10} cycloalkylalkyl, C_{6-12} cycloalkylalkyl, or C_{6-9} cycloalkylalkyl. For example, C_{6-9} cycloalkylalkyl includes a C_{1-3} alkyl group bonded to a cyclopentyl or a cyclohexyl group.

[033] "Cycloalkylalkanediyl" refers to a diradical of a cycloalkylalkane group. In certain embodiments, the cycloalkylalkanediyl group is C_{4-16} cycloalkylalkanediyl, C_{4-12} cycloalkylalkanediyl, C_{4-10} cycloalkylalkanediyl, C_{6-12} cycloalkylalkanediyl, or C_{6-9} cycloalkylalkanediyl. For example, C_{6-9} cycloalkylalkanediyl includes a C_{1-3} alkyl group bonded to a cyclopentyl or a cyclohexyl group.

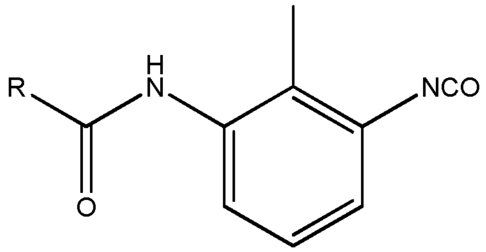
[034] "Cycloalkylalkane" group refers to a saturated, branched or straight-chain, acyclic hydrocarbon group in which one of the hydrogen atoms is replaced with a cycloalkane group. In certain embodiments of the cycloalkylalkane group, a hydrogen atom on the terminal carbon atom of a linear alkane group is replaced with a cycloalkyl group. In certain embodiments the cycloalkyl group is a C_{3-6} cycloalkyl group, in certain embodiments a C_{5-6} cycloalkyl group, and in certain embodiments a cyclopropyl, a cyclobutyl, a cyclopentyl, or a cyclohexyl group. The alkane portion of a cycloalkylalkane group may be, for example, C_{1-10} alkane, C_{1-6} alkane, C_{1-4} alkane, C_{1-3} alkane, propane, ethane, or methane. In certain embodiments, a cycloalkylalkane

group is C_{4-16} cycloalkylalkane, C_{4-12} cycloalkylalkane, C_{4-10} cycloalkylalkane, C_{6-12} cycloalkylalkane, or C_{6-9} cycloalkylalkane. For example, C_{6-9} cycloalkylalkane includes a C_{1-3} alkyl group bonded to a cyclopentyl or a cyclohexyl group.

[035] "Group derived from a diisocyanate" refers to a group in which one or both of the terminal isocyanate groups of a parent diisocyanate form a urethane (–O–C(O)–N(R)–), thiourethane (–S–C(O)–N(R)–), or urea linkage (–N(R)–C(O)–N(R)–). The group derived from a diisocyanate includes groups derived from aliphatic diisocyanates and groups derived from aromatic diisocyanates. In certain embodiments, the group derived from a diisocyanate is a group derived from an aliphatic diisocyanate, and in certain embodiments a group derived from a diisocyanate is a group derived from an aromatic diisocyanate. For example, a compound derived from 2,6-diisocyanatotoluene has the structure:



or



where each R is a bond to a –O–, –S–, or –NR– group.

[036] Examples of aliphatic diisocyanates include, 1,6-hexamethylene diisocyanate, 1,5-diisocyanato-2-methylpentane, methyl-2,6-diisocyanatohexanoate, bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane, 2,2,4-trimethylhexane 1,6-diisocyanate, 2,4,4-trimethylhexane 1,6-diisocyanate, 2,5(6)-bis(isocyanatomethyl)cyclo[2.2.1.]heptane, 1,3,3-trimethyl-1-(isocyanatomethyl)-5-isocyanatocyclohexane, 1,8-diisocyanato-2,4-dimethyloctane, octahydro-4,7-methano-1H-indenedimethyl diisocyanate, and 1,1'-methylenebis(4-isocyanatocyclohexane), and 4,4-methylene dicyclohexyl diisocyanate (H_{12}MDI).

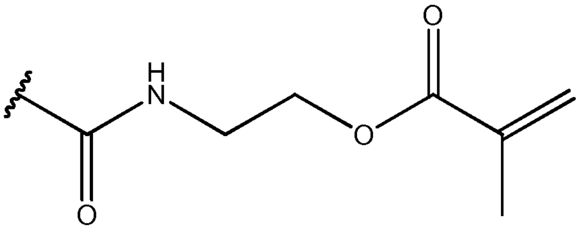
Examples of aromatic diisocyanates include 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate (2,6-TDI), 2,4-toluene diisocyanate (2,4-TDI), a blend of 2,4-TDI and 2,6-TDI, 1,5-diisocyanatonaphthalene, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate (4,4-MDI), 2,4'-methylenediphenyl diisocyanate (2,4-MDI), 2,2'-diisocyanatodiphenylmethane (2,2-MDI), diphenylmethane diisocyanate (MDI), 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl benzene, and 2,4,6-triisopropyl-m-phenylene diisocyanate.

[037] Examples of aromatic diisocyanates in which the isocyanate groups are not bonded directly to the aromatic ring include, bis(isocyanatoethyl)benzene, α, α, α',α'-tetramethylxylene diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene, bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene, bis(isocyanatomethyl)diphenyl ether, bis(isocyanatoethyl)phthalate, and 2,5-di(isocyanatomethyl)furan. Aromatic diisocyanates having isocyanate groups bonded directly to the aromatic ring include phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, 4,4'-diphenylmethane diisocyanate, bis(3-methyl-4-isocyanatophenyl)methane, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxy-biphenyl-4,4'-diisocyanate, diphenylether diisocyanate, bis(isocyanatophenylether)ethyleneglycol, bis(isocyanatophenylether)-1,3-propyleneglycol, benzophenone diisocyanate, carbazole diisocyanate, ethylcarbazole diisocyanate, dichlorocarbazole diisocyanate, 4,4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, 2,4-toluene diisocyanate, and 2,6-toluene diisocyanate.

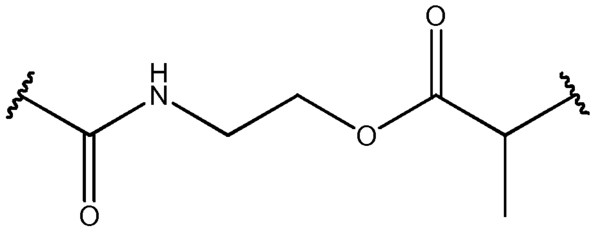
[038] Examples of alicyclic diisocyanates include isophorone diisocyanate, cyclohexane diisocyanate, methylcyclohexane diisocyanate, bis(isocyanatomethyl)cyclohexane, bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-

heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane, and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-isocyanatoethyl)-bicyclo[2.2.1]-heptane.

[039] "Group derived from an ethylenically unsaturated monoisocyanate" refers to a group in which the isocyanate group of a parent ethylenically unsaturated monoisocyanate forms a urethane, thiourethane or urea linkage and the ethylenically unsaturated group is bonded to another moiety or that is not bonded to another moiety. In certain embodiments, a group derived from an ethylenically unsaturated isocyanate refers to a group in which an isocyanate group of a parent ethylenically unsaturated monoisocyanate forms a urethane, thiourethane or urea linkage and the ethylenically unsaturated group is not bonded to another moiety. For example, a group derived from the ethylenically unsaturated monoisocyanate 2-isocyanatoethyl methacrylate can have the structure:



where the carbonyl is bonded to –O–, –S–, or –NR– to form a urethane, thiourethane or urea group, respectively. In certain embodiments, a group derived from an ethylenically unsaturated isocyanate refers to a group in which an isocyanate group of a parent ethylenically unsaturated monoisocyanate forms a urethane, thiourethane or urea linkage and the ethylenically unsaturated group is bonded to another moiety. In such embodiments, a group derived from the ethylenically unsaturated monoisocyanate 2-isocyanatoethyl methacrylate has the structure:



where the carbonyl is bonded to –O–, –S–, or –NR– to form a urethane, thiourethane or urea group, and the former vinyl group is bonded to another moiety.

[040] "Heteroalkanearene" refers to an alkanearene group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkanearene, a heteroatom is selected from N and O.

[041] "Heteroalkanearenediyl" refers to an alkanearenediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkanearenediyl, the heteroatom is selected from N and O.

[042] "Heteroalkanecycloalkane" refers to an alkanecycloalkane group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkanecycloalkane, the heteroatom is selected from N and O.

[043] "Heteroalkanecycloalkanediyl" refers to an alkanecycloalkanediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkanecycloalkanediyl, the heteroatom is selected from N and O.

[044] "Heteroalkanediyl" refers to an alkanediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkanediyl, the heteroatom is selected from N and O.

[045] "Heterocycloalkanediyl" refers to a cycloalkanediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heterocycloalkanediyl, the heteroatom is selected from N and O.

[046] "Heteroalkyl" refers to an alkyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroalkyl, the heteroatom is selected from N and O.

[047] "Heteroarenediyl" refers to an arenediyl group in which one or more of the carbon atoms are replaced with a heteroatom, such as N, O, S, or P. In certain embodiments of heteroarenediyl, the heteroatom is selected from N and O.

[048] "Heteroaryl" refers to a monovalent heteroaromatic radical derived by the removal of one hydrogen atom from a single atom of a parent heteroaromatic ring system. Heteroaryl encompasses multiple ring systems having at least one heteroaromatic ring fused to at least one other ring, which can be aromatic or non-aromatic. Heteroaryl encompasses 5- to 7-membered aromatic, monocyclic rings containing one or more, for example, from 1 to 4, or in certain embodiments, from 1 to 3, heteroatoms chosen from N, O, S, and P with the remaining ring atoms being carbon; and bicyclic heterocycloalkyl rings containing one or more, for example, from 1 to 4, or in certain embodiments, from 1 to 3, heteroatoms chosen from N, O, S, and P, with the remaining ring atoms being carbon and wherein at least one heteroatom is present in an aromatic ring. For example, heteroaryl includes a 5- to 7-membered heteroaromatic ring fused to a 5- to 7-membered cycloalkyl ring. For such fused, bicyclic heteroaryl ring systems wherein only one of the rings contains one or more heteroatoms, the point of attachment may be at the heteroaromatic ring or the cycloalkyl ring. In certain embodiments, where the total number of N, O, S, and P atoms in the heteroaryl group exceeds one, the heteroatoms are not adjacent to one another. In certain embodiments, the total number of N, O, S, and P atoms in the heteroaryl group is not more than two. In certain embodiments, the total number of N, O, S, and P atoms in the aromatic heterocycle is not more than one. Heteroaryl does not encompass or overlap with aryl as defined herein. Examples of heteroaryl groups include, but are not limited to, groups derived from acridine, arsindole, carbazole, α-carboline, chromane, chromene, cinnoline, furan, imidazole, indazole, indole, indoline, indolizine, isobenzofuran, isochromene, isoindole, isoindoline, isoquinoline, isothiazole, isoxazole, naphthyridine, oxadiazole, oxazole, perimidine, phenanthridine, phenanthroline, phenazine, phthalazine, pteridine, purine, pyran, pyrazine, pyrazole, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolizine, quinazoline, quinoline, quinolizine, quinoxaline, tetrazole, thiadiazole, thiazole, thiophene, triazole, xanthene, and the like. In certain embodiments, a heteroaryl group is C_{5-20} heteroaryl, C_{5-12} heteroaryl, C_{5-10} heteroaryl, and in certain embodiments C_{5-6}

heteroaryl. In certain embodiments heteroaryl groups are those derived from thiophene, pyrrole, benzothiophene, benzofuran, indole, pyridine, quinoline, imidazole, oxazole, or pyrazine.

[049] "Ketone" refers to a compound of the formula $CO(R)_2$, where each R is a hydrocarbon group. In certain embodiments of a ketone, each R is independently selected from C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, and substituted C_{6-12} cycloalkylalkyl. In certain embodiments of the ketone, each R is independently selected from methyl, ethyl, and propyl. In certain embodiments, the ketone is selected from propan-2-one, butan-2-one, pentan-2-one, and pentan-3-one.

[050] "Phenylalkyl" refers to an alkyl group in which one of the hydrogen atoms is replaced with a phenyl group. In certain embodiments of phenylalkyl, one of the hydrogen atoms of the terminal carbon atom of a linear alkyl group is replaced with a phenyl group. In certain embodiments, the phenylalkyl group is C_{7-12} phenylalkyl, C_{7-10} phenylalkyl, C_{7-9} phenylalkyl, and in certain embodiments, benzyl.

[051] "Substituted" refers to a group in which one or more hydrogen atoms are each independently replaced with the same or different substituent(s). In certain embodiments, the substituent is selected from halogen, $-S(O)_2OH$, $-S(O)_2$, –SH, –SR where R is C_{1-6} alkyl, –COOH, $-NO_2$, $-NR_2$ where each R is independently selected from hydrogen and C_{1-3} alkyl, –CN, =O, C_{1-6} alkyl, $-CF_3$, –OH, phenyl, C_{2-6} heteroalkyl, C_{5-6} heteroaryl, C_{1-6} alkoxy, and –COR where R is C_{1-6} alkyl. In certain embodiments, the substituent is chosen from –OH, $-NH_2$, and C_{1-3} alkyl.

[052] For purposes of the following description, it is to be understood that embodiments provided by the present disclosure may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in the examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the

claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[053] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[054] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges encompassed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of about 1 and the recited maximum value of about 10, that is, having a minimum value equal to or greater than about 1 and a maximum value of equal to or less than about 10.

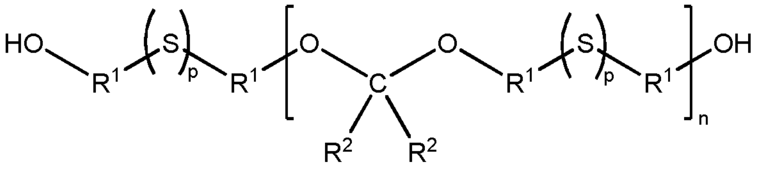
[055] Reference is now made to certain embodiments of polymers, compositions, and methods. The disclosed embodiments are not intended to be limiting of the claims. To the contrary, the claims are intended to cover all alternatives, modifications, and equivalents.

Difunctional Sulfur-Containing Polymers

[056] As indicated, certain embodiments provided by the present disclosure relate to terminal-modified sulfur-containing polymers. Sulfur-containing polymers include polythioethers, polydisulfides, and polymers containing both thioether and disulfide groups. Polythioether generally refers to a polymer containing at least two thioether groups, *e.g.*, two –C–S–C–groups. Polydisulfide refers to a polymer containing at least two disulfide groups, *e.g.*, two –C–S–S–C– groups. In addition to at least two thioether and/or disulfide groups, sulfur-containing polymers provided by the present disclosure comprise at least two formal, acetal, and/or ketal groups, *e.g.*, at least two $–O–C(R)_2–O–$ groups, where each R is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl. As used herein, "polymer" refers to oligomers, homopolymers, and copolymers. Unless stated otherwise, molecular weights are number average molecular weights for polymeric materials indicated as

"Mn" as determined, for example, by gel permeation chromatography using a polystyrene standard in an art-recognized manner.

[057] In certain embodiments, a difunctional sulfur-containing polymer has the structure of Formula (I):



(I)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl. Each R^1 may be the same or may be different, and each R^2 may be the same or may be different.

[058] In certain embodiments of a sulfur-containing polymer of Formula (I), each R^1 is independently selected from C_{2-6} alkanediyl, C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments, ethane-1,2-diyl. In certain embodiments of a sulfur-containing polymer of Formula (I), each R^1 is ethane-1,2-diyl.

[059] In certain embodiments of a sulfur-containing polymer of Formula (I), each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{1-4} alkyl, C_{1-3} alkyl, and in certain embodiments, C_{1-2} alkyl. In certain embodiments of a sulfur-containing polymer of Formula (I), each R^2 is methyl, and in certain embodiments, ethyl. In certain embodiments of a sulfur-containing polymer of Formula (I), each R^2 is hydrogen, and in certain embodiments, each R^2 is selected from hydrogen, methyl, and ethyl.

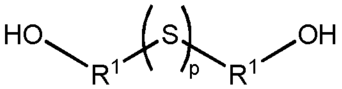
[060] In certain embodiments of a sulfur-containing polymer of Formula (I), each R^1 is the same and is selected from a C_{2-3} alkanediyl such as ethane-1,2-diyl and propane-1,3-diyl; and each R^2 is the same and is selected from hydrogen and C_{1-3} alkyl such as methyl, ethyl, and propyl. In certain embodiments of a sulfur-containing polymer of Formula (I), each R^2 is hydrogen, and in certain embodiments, each R^2 is methyl. In certain embodiments of a sulfur-containing polymer of Formula (I), each

R^1 is ethane-1,2-diyl and each R^2 is hydrogen. In certain embodiments of a sulfur-containing polymer of Formula (I), each R^1 is the same and is selected from ethane-1,2-diyl and propane-1,3-diyl; and each R^2 is independently selected from hydrogen, methyl, and ethyl.

[061] In certain embodiments of a sulfur-containing polymer of Formula (I), n is an integer selected from 1 to 50, an integer selected from 2 to 40, an integer selected from 4 to 30, and in certain embodiments, n is an integer selected from 7 to 30.

[062] In certain embodiments of a sulfur-containing polymer of Formula (I), each p is the same and is 1, and in certain embodiments, each p is the same and is 2.

[063] In certain embodiments, a sulfur-containing polymer of Formula (I) comprises the reaction products of (i) a sulfur-containing diol; and (ii) a reactant selected from an aldehyde, a ketone, and a combination thereof. In certain embodiments of the reaction, the sulfur-containing diol comprises the structure:



where p is selected from 1 and 2; and each R^1 is independently selected from C_{2-6} alkanediyl. In certain embodiments of a sulfur-containing diol, p is 1 and in certain embodiments p is 2. In certain embodiments of a sulfur-containing diol, each R^1 is the same and in certain embodiments, each R^1 is different. In certain embodiments, each R^1 is selected from C_{2-5} alkanediyl, C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments, R^1 is ethane-1,2-diyl. In certain embodiments of the reaction, the sulfur-containing diol comprises a sulfur-containing diol selected from 2,2'-thiodiethanol, 3,3'-thiobis(propan-1-ol), 4,4'-thiobis(butan-1-ol), and a combination of any of the foregoing. In certain embodiments of the reaction, the sulfur-containing diol comprises 2,2'-thiodiethanol.

[064] In certain embodiments of the reaction, the sulfur-containing diol comprises a single type of sulfur-containing diol, and in certain embodiments, comprises a mixture of sulfur-containing diols. A mixture of sulfur-containing diols may comprise from 5 mol% to 95 mol% of one or more thioethers (p is 1) and from 95 mol% to 5 mol% of one or more disulfides (p is 2). In certain embodiments, a

mixture of sulfur-containing diols comprises 50 mol% of one or more thioethers and 50 mol% of one or more disulfides. In certain embodiments, a mixture of sulfur-containing diols comprises from 0 mol% to 30 mol% of one or more disulfides, and from 100 mol% to 70 mol% of one or more thioethers.

[065] In certain embodiments of the reaction, reactant (ii) is an aldehyde. In certain embodiments in which reactant (ii) is an aldehyde, the aldehyde comprises a C_{1-6} aldehyde, a C_{1-4} aldehyde, a C_{1-3} aldehyde, and in certain embodiments, a C_{1-2} aldehyde. In certain embodiments, the aldehyde is formaldehyde.

[066] In certain embodiments of the reaction, reactant (ii) is a ketone. In certain embodiments in which reactant (ii) is a ketone, the ketone has the formula COR_2 where each R^2 is independently selected from C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl. In certain embodiments of a ketone, each R^2 is independently selected from methyl, ethyl, and propyl. In certain embodiments, a ketone is selected from propan-2-one, butan-2-one, pentan-2-one, and pentan-3-one.

[067] In certain embodiments, a sulfur-containing polymer of Formula (I) is the reaction products of reactants comprising 2,2'-thiodiethanol and formaldehyde, and is referred to herein as thiodiglycol polythioether or thiodiglycol polyformal.

[068] The reaction used to prepare a sulfur-containing polymer of Formula (I) may take place in the presence of an acidic catalyst, such as sulfuric acid, sulfonic acid, or a combination thereof. In certain embodiments, a sulfonic acid may be used. Examples of sulfonic acids include alkyl sulfonic acids such as methane sulfonic acid, ethane sulfonic acid *tert*-butane sulfonic acid, 2-propane sulfonic acid, and cyclohexyl sulfonic acid; alkene sulfonic acids such as α-olefin sulfonic acid, dimerized α-olefin sulfonic acid, and 2-hexene sulfonic acid; aromatic sulfonic acids such as para-toluene sulfonic acids, benzene sulfonic acid, and naphthalene sulfonic acid; and polymer-supported sulfonic acids such as AMBERLYST™ sulfonic acid catalysts available from Dow Chemical.

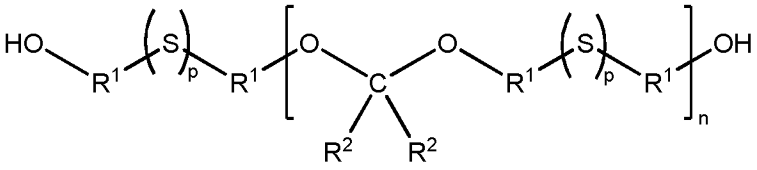
[069] In certain embodiments, sulfur-containing polymers of Formula (I) have a hydroxyl number from 10 to 100, from 20 to 80, from 20 to 60, from 20 to 50, and in certain embodiments, from 20 to 40. The hydroxyl number is the hydroxyl

content of the sulfur-containing polymer, and may be determined, for example, by acetylating the hydroxyl groups and titrating the resultant acid against potassium hydroxide. The hydroxyl number is the weight of potassium hydroxide in milligrams that will neutralize the acid from one gram of the sulfur-containing polymer.

[070] In certain embodiments, a sulfur-containing polymer of Formula (I) has a number average molecular weight from 200 to 6,000 Daltons, from 500 to 5,000 Daltons, from 1,000 to 5,000 Daltons, from 1,500 to 4,000 Daltons, and in certain embodiments, from 2,000 to 3,600 Daltons.

Terminal-Modified Difunctional Sulfur-Containing Polymers

[071] In certain embodiments, a terminal-modified sulfur-containing polymer comprises the reaction products of reactants comprising: (a) a sulfur-containing polymer of Formula (I):



(I)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (b) a compound comprising a terminal group selected from a vinyl group, a silyl group, and an epoxy group; and a group that is reactive with the terminal hydroxyl groups of the polymer of Formula (I).

[072] In certain embodiments of a terminal-modified sulfur-containing polymer, the terminal group is a vinyl group and the compound comprising a terminal vinyl group is selected from an ethylenically unsaturated isocyanate and an ethylenically unsaturated alcohol.

[073] An ethylenically unsaturated isocyanate includes ethylenically unsaturated monoisocyanate and ethylenically unsaturated diisocyanates such as ethylenically unsaturated aromatic monoisocyanates, ethylenically unsaturated

aliphatic monoisocyanates, ethylenically unsaturated aromatic diisocyanates, and ethylenically unsaturated aliphatic diisocyanates.

[074] Examples of ethylenically unsaturated diisocyanates include butene diisocyanate and 1,3-butadiene-1,4-diisocyanate.

[075] Examples of ethylenically unsaturated monoisocyanates include vinyl isocyanate, allyl isocyanate, 3-isocyanato-2-methyl-2-propene, methacryloyl isocyanate, isocyanatoethyl methacrylate, vinyl-benzyl isocyanate, 3-isocyanato-1-butene, 3-isocyanato-3-methyl-1-butene, 4-isocyanato-2-methyl-1-butene, 4-isocyanato-3,3-dimethyl-1-butene, 4-isocyanato-4-methyl-1-pentene, and 5-isocyanato-1-pentene, 2-isocyanatoethyl methacrylate, and dimethyl-meta-isopropenylbenzyl isocyanate (TMI). In certain embodiments, an ethylenically unsaturated monoisocyanate is selected from vinyl isocyanate, allyl isocyanate, and methyacryloyl isocyanate. In certain embodiments, an ethylenically unsaturated aliphatic isocyanate is C_{2-10} alkenyl isocyanate, C_{2-8} alkenyl isocyanate, C_{2-6} alkenyl isocyanate, and in certain embodiments, C_{2-3} alkenyl isocyanate.

[076] Examples of ethylenically unsaturated alcohols include, for example, allyl alcohol, 3-buten-1-ol, 3-buten-2-ol, ethylene glycol monovinyl ether, ethylene glycol monoallyl ether, diethylene glycol monoallyl ether, glycerin monoallyl ether, trimethylolethane monoallyl ether, trimethylolpropane monoallyl ether, polyethylene glycol monoallyl ether, polypropylene glycol monoallyl ether, 1-vinylcyclobutanol, 2-vinylcyclobutanol, 3-vinylcyclobutanol, vinylphenol, 2-allyl phenol, 4-allylphenol, 4-allyl-2-methoxyphenol, 4-allyl-2,6-dimethoxyphenol, 4-(2-propenyl)-1,2-benzenediol, and 4-(2,4-dihydroxyphenyl)-3-buten-2-one. In certain embodiments, an ethylenically unsaturated alcohol is selected from allyl alcohol, ethylene glycol monoallyl ether, 2-allylphenol, and 4-allylphenol.

[077] In certain embodiments, the compound comprising a vinyl group is an ethylenically unsaturated isocyanate and is selected from 3-isopropenyl-α,α-dimethylbenzyl isocyanate (CAS 2094-99-7) and 2-isocyanatoethyl methacrylate.

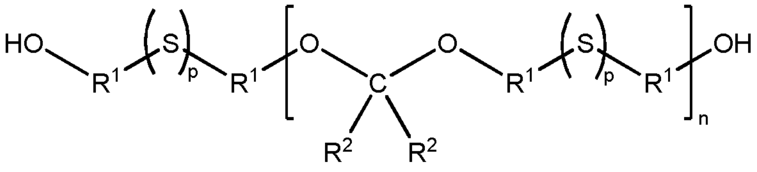
[078] In certain embodiments of a reaction to form a terminal-modified sulfur-containing polymer, the terminal group is a silyl group and the compound comprising a terminal silyl group is an isocyanatoalkylalkoxysilane. Examples of suitable isocyanatoalkylalkoxysilanes include, for example,

isocyanatopropylmethoxysilane, isocyanatopropylmethyldimethoxysilane, isocyanatopropylmethyldiethoxysilane, isocyanatopropyltriethoxysilane, isocyanatopropyltriisopropoxysilane, isocyanatopropylmethyldiisopropoxysilane, isocyanatoneohexyltrimethoxysilane, isocyanatoneohexyldimethoxysilane, isocyanatoneohexyldiethoxysilane, isocyanatoneohexyltriethoxysilane, isocyanatoneohexyltriisopropoxysilane, isocyanatoneohexyldiisopropoxysilane, isocyanatoisoamyltrimethoxysilane, isocyanatoisoamyldimethoxysilane, isocyanatoisoamylmethylsilane, isocyanatoisoamylmethyldiethoxysilane, isocyanatoisoamyltriethoxysilane, isocyanatoisoamyltriisopropoxysilane, and isocyanatoisoamylmethyldiisopropoxysilane. In certain embodiments, the isocyanatoalkyltrialkoxysilane is 3-isocyanatopropyltrimethoxysilane.

[079] In certain embodiments of a reaction to form a terminal-modified sulfur-containing polymer, the terminal group is an epoxy group and the compound comprising a terminal epoxy group is selected from C_{1-6} epoxy alkanol, C_{1-6} epoxy haloalkane, and a combination thereof. Examples of suitable C_{1-6} alkanol epoxides include oxirane-2-ol, oxirane-2-ylmethanol, and 2-(oxirane-2-yl)ethanol. Examples of suitable C_{1-6} epoxy haloalkanes include, for example, 2-(chloromethyl)oxirane and 2-(2-chloroethyl)oxirane.

[080] In certain embodiments, a terminal-modified sulfur-containing polymer comprises the reaction products of reactants comprising: (a) and (b), wherein (a) comprises the reaction products of reactants comprising (i) and (ii), wherein (i) comprises a sulfur-containing polymer of Formula (I), wherein n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (ii) comprises a first compound selected from a diisocyanate, an ethylenically unsaturated isocyanate, and a tosylate; and (b) comprises a second compound comprising a terminal group selected from a vinyl group, a silyl group, and an epoxy group; and a group selected from a group that is reactive with an isocyanate group, a group that is reactive with an ethylenically unsaturated group, and a a group that is reactive with tosylate.

[081] In certain embodiments, an amine-terminated sulfur-containing polymer comprises the reaction products of reactants comprising (a) and (b), where (a) comprises the reaction products of reactants comprising: (i) and (ii), where (i) comprises a sulfur-containing polymer of Formula (I):



(I)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (ii) comprises a first compound selected from a diisocyanate, an ethylenically unsaturated isocyanate, and a tosylate; and (b) comprises a second compound comprising a terminal amine group and a group selected from a group that is reactive with an isocyanate group, a group that is reactive with an ethylenically unsaturated group, and a group that is reactive with a tosylate.

[082] Examples of diisocyanates include, for example, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 2,6-toluene diisocyanate (2,6-TDI), 2,4-toluene diisocyanate (2,4-TDI), a blend of 2,4-TDI and 2,6-TDI, 1,5-diisocyanato naphthalene, diphenyl oxide 4,4'-diisocyanate, 4,4'-methylenediphenyl diisocyanate (4,4-MDI), 2,4'-methylenediphenyl diisocyanate (2,4-MDI), 2,2'-diisocyanatodiphenylmethane (2,2-MDI), diphenylmethane diisocyanate (MDI), 3,3'-dimethyl-4,4'-biphenylene isocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 1-[(2,4-diisocyanatophenyl)methyl]-3-isocyanato-2-methyl benzene, 2,4,6-triisopropyl-m-phenylene diisocyanate, and 4,4-methylene dicyclohexyl diisocyanate (H_{12}MDI). Other examples of diisocyanates are disclosed herein.

[083] In certain embodiments of the reaction to form a terminal-modified sulfur-containing polymer, the first compound is 2-isocyanatoethyl methacrylate.

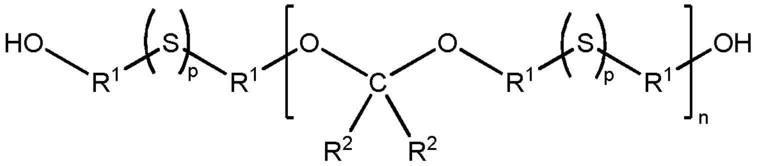
[084] Examples of ethylenically unsaturated isocyanates are disclosed herein.

[085] In certain embodiments, the tosylate is a sulfonyl chloride such as p-toluenesulfonyl chloride.

[086] In certain embodiments of a reaction to form a terminal-modified sulfur-containing polymer, the second compound comprising a terminal amine group is selected from aniline, an aminoalkyl-substituted aniline, an aminoalkyl, and a sulfur-containing diamine. In certain embodiments, an aminoalkyl-substituted aniline is selected from 4-(aminomethyl)aniline and 4-(aminoethyl)aniline. In certain embodiments an aminoalkyl is selected from ethanamine, propan-1-amine, and butan-1-amine. Suitable sulfur-containing diamines include, for example, ETHACURE® 300.

[087] In certain embodiments of a reaction to form a terminal-modified sulfur-containing polymer, the terminal group is an amine group and the compound comprising a terminal amine group is an alkyl-aminobenzoate. Examples of suitable alkylaminobenzoates include, for example, methyl 4-aminobenzoate, ethyl 4-aminobenzoate, methyl 3-aminobenzoate, ethyl 3-aminobenzoate, methyl 2-aminobenzoate, and ethyl 3-aminobenzoate. In certain embodiments, an alkyl-aminobenzoate is ethyl 4-aminobenzoate.

[088] In certain embodiments, a thiol-terminated sulfur-containing polymer comprises the reaction products of reactants comprising: (a) and (b), where (a) comprises the reaction products of reactants comprising (i) and (ii), where (i) comprises a sulfur-containing polymer of Formula (I):



(I)

where n is an integer selected from 1 to 50; and each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; and each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and (ii) comprises a first compound selected from a diisocyanate, thiourea, an ethylenically unsaturated isocyanate, and a tosylate; and (b) comprises a mercaptoalkanol when (ii) comprises a diisocyanate; (b) comprises a metal hydrosulfide when (ii) comprises thiourea; (b) comprises a dithiol when (ii) comprises an ethylenically unsaturated isocyanate; and (b) comprises a metal hydrosulfide when (ii) comprises a tosylate.

[089] Examples of suitable diisocyanates include, for example, those described herein. Examples of suitable ethylenically unsaturated isocyanates include, for example, those described herein.

[090] In certain embodiments of a reaction to form a terminal-modified sulfur-containing polymer, the terminal group is a thiol group and the compound comprising a terminal thiol group is selected from a dithiol and an alkyl(bis)oxydialkanethiol. Examples of suitable dithiols include compounds of the formula HS–R–SH where R is a C_{2-6} alkanediyl, having one or more pendant groups, which can be, for example, hydroxyl groups, C_{1-6} alkyl groups such as methyl or ethyl groups; C_{1-6} alkoxy, C_{6-8} cycloalkanediyl, C_{6-10} alkanecycloalkanediyl, $–[–(CH_2)_p–X–]_q–(CH_2)_r–$, or $–[–(CH_2)_p–X–]_q–(CH_2)_r–$ in which at least one $–CH_2–$ unit is substituted with a methyl group and in which each p is independently selected from an integer selected from 2 to 6, each q is independently selected from an integer selected from 1 to 5, and each r is independently selected from an integer selected from 2 to 10. Dithiols may include one or more heteroatom substituents in the carbon backbone, for example, dithiols in which X includes a heteroatom such as O, S or other bivalent heteroatom radical, a secondary or tertiary amine group such as –NR'–, where R' is hydrogen or methyl, or another substituted trivalent heteroatom. In certain embodiments, X is O or S, and in certain embodiments, p and r are equal, and in certain embodiments both p and r are 2. In certain embodiments, X is a bond. Examples of suitable dithiols include 1,2-ethanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 1,3-butanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,3-pentanedithiol, 1,5-pentanedithiol, 1,6-hexanedithiol, 1,3-dimercapto-3-methylbutane, dipentenedimercaptan, ethylcyclohexyldithiol, dimercaptodiethylsulfide, methyl-substituted dimercaptodiethylsulfide, dimethyl-substituted dimercaptodiethylsulfide, dimethyl-substituted dimercaptodiethylsulfide, dimercaptodioxaoctane, and 1,5-dimercapto-3-oxapentane. A dithiol may have one or more pendant groups selected from C_{1-4} alkyl, C_{1-4} alkoxy, and hydroxyl. Additional examples of suitable

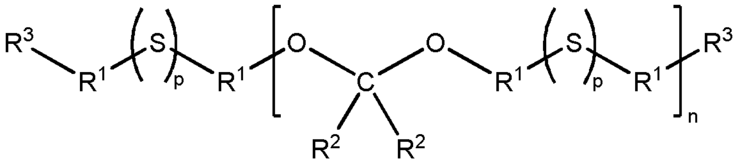
mercaptoalkanols include, for example, C_{2-6} mercaptoalkanols such as 2-mercaptoethan-1-ol, 3-mercaptopropan-1-ol, 4-mercaptobutan-1-ol, 5-mercaptopentan-1-ol, and 6-mercaptohexan-1-ol. Examples of suitable dithiols include, for example, C_{2-10} alkanedithiols such as ethane-1,2-dithiol, propane-1,3-dithiol, butane-1,4-dithiol, pentane-1,5-dithiol, and hexane-1,6-dithiol.

[091] In certain embodiments, a dithiol is an alkyl(bis)oxydialkane. Alkyl(bis)oxydialkane thiols may have the general formula HS–R–O–R'–O–R–HS, where each R and R' is an alkanediyl such as, for example, C_{2-6} alkanediyl, C_{2-4} alkanediyl, or C_2 alkanediyl. In certain embodiments, a dithiol is selected from dimercaptodiethylsulfide (DMDS), 1,8-dimercapto-3,6-dioxaoctane (DMDO), and 1,5-dimercapto-3-oxapentane.

[092] In certain embodiments, a metal hydrosulfide is sodium hydrosulfide. In certain embodiments, a tosylate is a sulfonyl chloride such as p-toluenesulfonyl chloride.

[093] In certain embodiments of the above terminal-modified sulfur-containing polymers, the terminal-modified sulfur-containing polymer has a number average molecular weight from 200 to 6,000 Daltons, from 500 to 5,000 Daltons, from 1,000 to 5,000 Daltons, from 1,500 to 4,000 Daltons, and in certain embodiments, from 2,000 to 3,600 Daltons.

[094] Certain terminal-modified sulfur-containing polymers provided by the present disclosure have the structure of Formula (II):



(II)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and each R^3 is $–OR^{3'}$

wherein $R^{3'}$ is selected from a vinyl-terminated group, a silyl-terminated group, an amine-terminated group, an epoxy-terminated group, and a thiol-terminated group.

[095] In certain embodiments of a sulfur-containing polymer of Formula (II), each R^1 is independently selected from C_{2-6} alkanediyl, C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments, ethane-1,2-diyl. In certain embodiments of a polymer of Formula (II), each R^1 is ethane-1,2-diyl.

[096] In certain embodiments of a sulfur-containing polymer of Formula (II), each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{1-4} alkyl, C_{1-3} alkyl, and in certain embodiments, C_{1-2} alkyl. In certain embodiments of a polymer of Formula (II), each R^2 is hydrogen, and in certain embodiments, methyl, and in certain embodiments ethyl.

[097] In certain embodiments of a sulfur-containing polymer of Formula (II), each R^1 is the same and is selected from a C_{2-3} alkanediyl such as ethane-1,2-diyl and propane-1,3-diyl; and each R^2 is the same and is selected from hydrogen and C_{1-3} alkyl such as methyl, ethyl, and propyl. In certain embodiments of a sulfur-containing polymer of Formula (II), each R^1 is ethane-1,2-diyl. In certain embodiments of a sulfur-containing polymer of Formula (II), each R^2 is hydrogen. In certain embodiments of a sulfur-containing polymer of Formula (II), each R^1 is ethane-1,2-diyl and each R^2 is hydrogen.

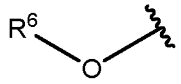
[098] In certain embodiments of a sulfur-containing polymer of Formula (II), n is an integer selected from 1 to 50, an integer selected from 2 to 40, an integer selected from 4 to 30, and in certain embodiments, n is an integer selected from 7 to 30.

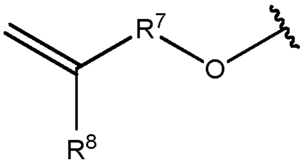
[099] In certain embodiments of a sulfur-containing polymer of Formula (II), each p is the same and is 1, and in certain embodiments, each p is the same and is 2.

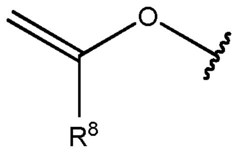
[0100] In certain embodiments, a sulfur-containing polymer of Formula (II) has a number average molecular weight from 200 to 6,000 Daltons, from 500 to 5,000 Daltons, from 1,000 to 5,000 Daltons, from 1,500 to 4000 Daltons, and in certain embodiments, from 2,000 to 3,600 Daltons.

[0101] In certain embodiments of a polymer of Formula (II), each R^3 is the same.

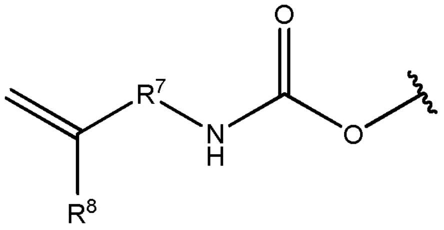
[0102] In certain embodiments of a polymer of Formula (II), each R^3 is a vinyl-terminated group and is independently selected from a group of Formula (a), Formula (b), Formula (c), Formula (d), and Formula (e):



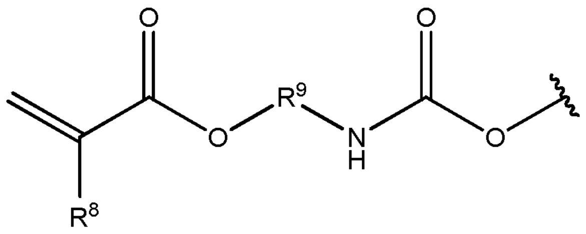




(a) (b) (c)



and



(d) (e)

where each R^6 is a moiety derived from an ethylenically unsaturated monoisocyanate; each R^7 is selected from C_{2-6} alkanediyl and C_{2-6} heteroalkanediyl; each R^8 is selected from hydrogen, C_{1-6} alkyl, and phenyl; and each R^9 is selected from C_{2-6} alkanediyl, C_{2-6} heteroalkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{6-12} heteroarenediyl, substituted C_{6-12} heteroarenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{3-12} heterocycloalkanediyl, substituted C_{3-12} heterocycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} heteroalkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

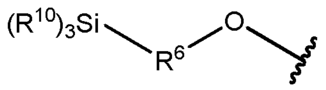
[0103] In certain embodiments, each R^6 is derived from an ethylenically unsaturated aliphatic monoisocyanate, an ethylenically unsaturated alicyclic monoisocyanate, and in certain embodiments, an ethylenically unsaturated aromatic monoisocyanate.

[0104] In certain embodiments of Formula (b) and Formula (d), each R^7 is selected from C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments is selected from ethane-1,2-diyl, propane-1,3-diyl, propane-1,2-diyl, and propane-1,1-diyl. In certain embodiments of Formula (b) and Formula (d), each R^7 is selected from ethane-1,2-diyl and propane-1,3-diyl.

[0105] In certain embodiments of Formula (b), Formula (c), Formula (d), and Formula (e), each R^8 is selected from hydrogen, methyl, ethyl, isopropyl, and n-propyl.

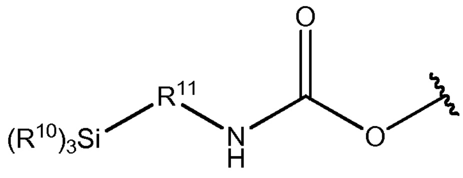
[0106] In certain embodiments of Formula (e), each R^9 is selected from C_{2-6} alkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} alkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl. In certain embodiments of Formula (e), each R^9 is the same and is selected from methane-diyl, ethane-1,2-diyl, and propane-1,2-diyl. In certain embodiments of Formula (e), each R^9 is C_{2-5} alkanediyl, C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments, ethane-1,2-diyl.

[0107] In certain embodiments of polymers of Formula (II), each R^3 is a silyl-terminated group of Formula (f) and Formula (g):



(f)

and

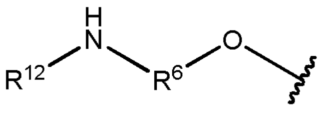


(g)

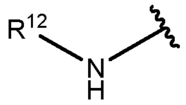
where each R^6 is derived from an ethylenically unsaturated monoisocyanate; each R^{10} is independently selected from C_{1-6} alkyl, C_{1-6} alkoxy, C_{5-6} cycloalkyl, C_{6-12} cycloalkylalkyl, phenyl, and C_{7-12} phenylalkyl; wherein at least one R^{10} is C_{1-6} alkoxy; and each R^{11} is C_{1-6} alkanediyl.

[0108] In certain embodiments of Formula (g), each R^{11} is selected from methane-diyl, ethane-1,2-diyl, and propane-1,2-diyl. In certain embodiments of Formula (f) and Formula (g), each R^{10} is the same and is selected from methoxy, ethoxy, and propoxy. In certain embodiments of Formula (f) and Formula (g), the silyl-terminal group is a trialkoxysilane, in certain embodiments, a dialkoxysilane, and in certain embodiments, a monoalkoxysilane.

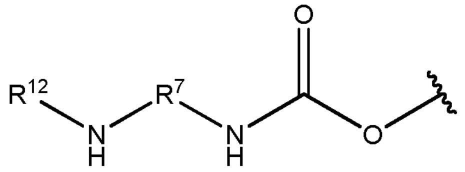
[0109] In certain embodiments of a polymer of Formula (II), each R^3 is an amine-terminated group and is independently selected from a group of Formula (h), Formula (i), Formula (j), Formula (k), Formula (l), and Formula (m):



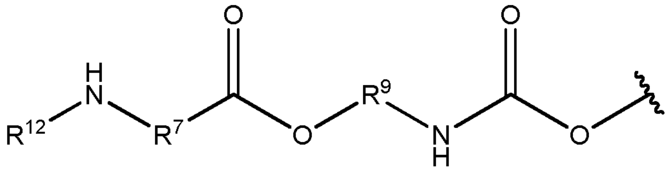
(h)



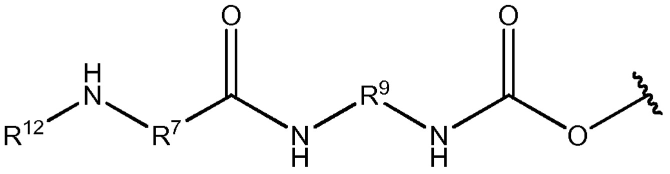
(i)



(j)

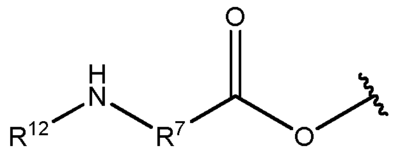


(k)



and

(l)



(m)

where each R^6 is selected from a group derived from a diisocyanate and a group derived from an ethylenically unsaturated monoisocyanate; each R^7 is selected from a bond and C_{2-6} alkanediyl; each R^9 is selected from C_{2-6} alkanediyl, C_{2-6} heteroalkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{6-12} heteroarenediyl, substituted C_{6-12} heteroarenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{3-12} heterocycloalkanediyl, substituted C_{3-12} heterocycloalkanediyl,

C_{7-18} alkanearenediyl, substituted C_{7-18} heteroalkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl; and each R^{12} is selected from hydrogen, C_{1-6} alkyl, C_{6-12} aryl, substituted C_{6-12} aryl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{7-18} arylalkyl, substituted C_{7-18} arylalkyl, C_{4-18} alkylcycloalkyl, and substituted C_{4-18} alkylcycloalkyl.

[0110] In certain embodiments of Formula (h), each R^6 is a group derived from a diisocyanate, and in certain embodiments the group is derived from TDI, ISONATE™ 143L (polycarbodiimide-modified diphenylmethane diisocyanate), DESMODUR® N3400 (1,3-diazetidine-2,4-dione, 1,3-bis(6-isocyanatohexyl)-), DESMODUR® (I) (isophorone diisocyanate, IPDI), of DESMODUR® W (H_{12}MDI).

[0111] In certain embodiments of Formula (h), each R^6 is a group derived from an ethylenically unsaturated monoisocyanate, and in certain embodiments is selected from 2-isocyanatoethyl methacrylate.

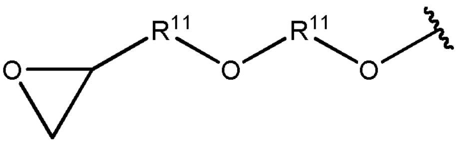
[0112] In certain embodiments of Formula (j), Formula (k), Formula (l), and Formula (m), each R^7 is selected from C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments is selected from ethane-1,2-diyl, propane-1,3-diyl, propane-1,2-diyl, and propane-1,1-diyl. In certain embodiments of Formula (j), Formula (k), Formula (l), and Formula (m), each R^7 is selected from ethane-1,2-diyl and propane-1,3-diyl.

[0113] In certain embodiments of Formula (k) and Formula (l), each R^9 is selected from C_{2-6} alkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} alkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

[0114] In certain embodiments of Formula (h), Formula (i), Formula (j), Formula (k), Formula (l), and Formula (m), each R^{12} is selected from C_{1-6} alkyl, phenyl, and amino-substituted phenyl. In certain embodiments of Formula (h), Formula (i), Formula (j), Formula (k), Formula (l), and Formula (m), each R^{12} is selected from phenyl, methyl, ethyl, propyl, methyl-phenyl, ethyl-phenyl, propyl-phenyl, benzyl, phenethyl, $-(CH_2)-$aniline, and aminophenyl.

[0115] In certain embodiments of a moiety of Formula (f), R^7 is $-CH(CH_3)-CH_2-$.

[0116] In certain embodiments of a polymer of Formula (II), each R^3 is an epoxy-terminated group and is a group of Formula (n):

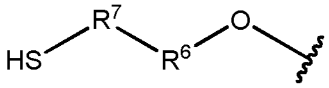


(n)

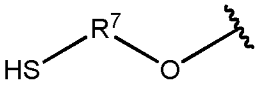
where each R^{11} is independently C_{1-6} alkanediyl.

[0117] In certain embodiments of Formula (n), each R^{11} is selected from methanediyl, ethane-1,2-diyl, and propane-1,3-diyl. In certain embodiments, each R^{11} is the same and is selected from methanediyl, ethane-1,2-diyl, and propane-1,3-diyl.

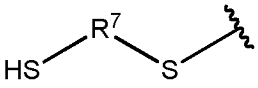
[0118] In certain embodiments of a polymer of Formula (II), each R^3 is a thiol-terminated group and is independently selected from a group of Formula (o), Formula (p), Formula (q), Formula (r), Formula (s), Formula (t), Formula (u), and Formula (v):



(o)

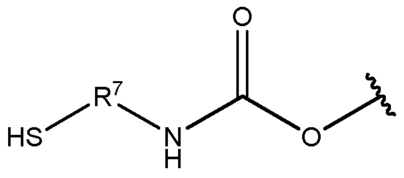


(p)

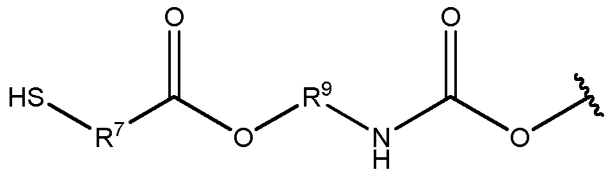


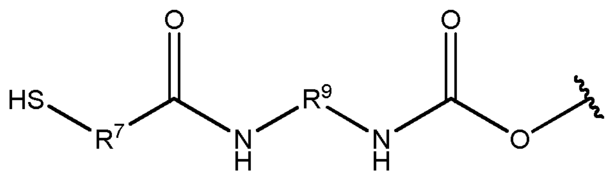
(q)

(r)



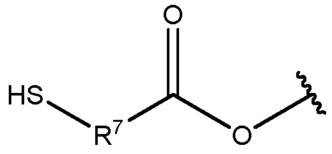
(s)





(t) (u)

and



(v)

where each R^6 is selected from a moiety derived from a diisocyanate and a moiety derived from an ethylenically unsaturated monoisocyanate; each R^7 is selected from C_{2-14} alkanediyl and C_{2-14} heteroalkanediyl; and each R^9 is selected from C_{2-6} alkanediyl, C_{2-6} heteroalkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{6-12} heteroarenediyl, substituted C_{6-12} heteroarenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{3-12} heterocycloalkanediyl, substituted C_{3-12} heterocycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} heteroalkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

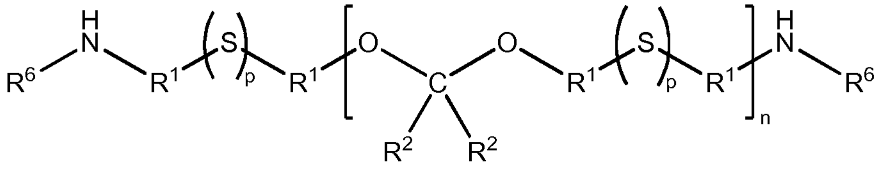
[0119] In certain embodiments of Formula (o), each R^6 is a group derived from a diisocyanate, and in certain embodiments the group is derived from TDI, ISONATE™ 143L (polycarbodiimide-modified diphenylmethane diisocyanate), DESMODUR® N3400 (1,3-diazetidine-2,4-dione, 1,3-bis(6-isocyanatohexyl)-), DESMODUR® I (isophorone diisocyanate, IPDI), or DESMODUR® W (H_{12}MDI).

[0120] In certain embodiments of Formula (o), each R^6 is a group derived from an ethylenically unsaturated monoisocyanate, and in certain embodiments is 2-isocyanatoethyl methacrylate.

[0121] In certain embodiments of Formula (o), Formula (p), Formula (q), Formula (s), Formula (t), Formula (u), and Formula (v), each R^7 is selected from C_{2-6} alkanediyl. In certain embodiments of Formula (o), Formula (p), Formula (q), Formula (s), Formula (t), Formula (u), and Formula (v), each R^7 is selected from $–CH_2–S–(CH_2)_2–O–(CH_2)_2–O–(CH_2)_2–$, $–(CH_2)_2–O–$ $(CH_2)_2–O–(CH_2)_2–$, and $–(CH_2)_2–S–(CH_2)_2–O–(CH_2)_2–O–(CH_2)_2–$.

[0122] In certain embodiments of Formula (t) and Formula (u), each R^9 is selected from C_{2-6} alkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} alkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

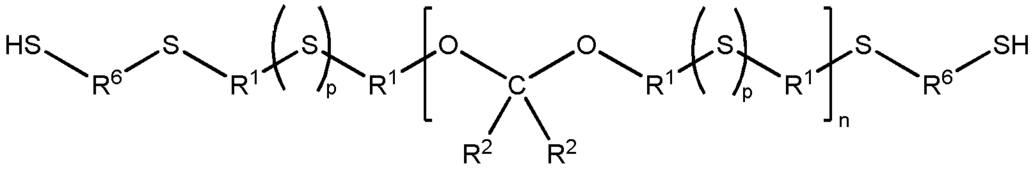
[0123] In certain embodiments, an amine-terminated sulfur-containing polymer has the structure of Formula (III):



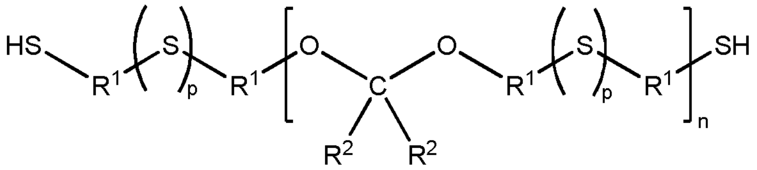
(III)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl, and each R^6 is independently selected from hydrogen, C_{5-6} cycloalkyl, phenyl, C_{1-6} alkyl. In certain embodiments of a polymer of Formula (III), each p is 1, and in certain embodiments each p is 2. In certain embodiments of a polymer of Formula (III), each R^1 may be the same or may be different. In certain embodiments of a polymer of Formula (III), each R^1 is C_{2-5} alkanediyl, C_{2-4} alkanediyl, C_{2-3} alkanediyl, and in certain embodiments, ethane-1,2-diyl. In certain embodiments of a polymer of Formula (III), each R^2 may be the same and in certain embodiments may be different. In certain embodiments of a polymer of Formula (III), each R^2 is hydrogen, C_{1-5} alkyl, C_{1-4} alkyl, n-propyl, isopropyl, ethyl, and in certain embodiments, methyl. In certain embodiments of a polymer of Formula (III), each R^1 is the same and is selected from ethane-1,2-diyl, propane-1,2-diyl and propane-1,3-diyl; and each R^2 is the same and is selected from hydrogen, methyl, and ethyl. In certain embodiments of a polymer of Formula (III), each R^6 is the same and is selected from hydrogen, cyclohexyl, phenyl, methyl, ethyl, and propyl. In certain embodiments of a polymer of Formula (III), n is an integer selected from 5 to 40, and in certain embodiments, an integer selected from 10 to 40.

[0124] In certain embodiments, a thiol-terminated sulfur-containing polymer is selected from Formula (IVa) and Formula (IVb):



(IVa)



(IVb)

where n is an integer selected from 1 to 50; each p is independently selected from 1 and 2; each R^1 is independently selected from C_{2-6} alkanediyl; each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted $_{7-12}$ phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and each R^6 is independently selected from C_{2-6} alkanediyl and C_{5-12} heteroalkanediyl. In certain embodiments of a polymer of Formulae (IVa) and (IVb), each p is 1 and in certain embodiments, each p is 2. In certain embodiments of a polymer of Formulae (IVa) and (IVb), each R^1 may be the same and in certain embodiments, R^1 may be different. In certain embodiments of a polymer of Formulae (IVa) and (IVb), each R^1 is C_{2-5} alkanediyl, C_{2-4} alkanediyl, propane-1,3-diyl, propane-1,2-diyl, and in certain embodiments, ethane-1,2-diyl. In certain embodiments of a polymer of Formulae (IVa) and (IVb), each R^1 is the same and is selected from ethane-1,2-diyl and propane-1,3-diyl, and each R^2 is the same and is selected from hydrogen, methyl, and ethyl. In certain embodiments of a polymer of Formulae (IVa), each R^6 is the same and is selected from ethane-1,2-diyl and propane-1,3-diyl. In certain embodiments of a polymer of Formulae (IVa) and (IVb), n is an integer selected from 5 to 40, and in certain embodiments, an integer selected from 10 to 40.

Synthesis of Sulfur-Containing Polymers

[0125] Difunctional sulfur-containing polymers provided by the present disclosure and precursors thereof may be prepared by a number of methods known to those skilled in the art, including those described in the examples herein. For example, to obtain difunctional sulfur-containing polymers of Formula (I), a sulfur-containing diol and an aldehyde and/or ketone may be reacted in an organic solvent in the presence of a sulfonic acid catalyst such as AMBERLYST™ 15 to provide the corresponding difunctional sulfur-containing polymer of Formula (I).

Synthesis of Terminal-Modified Difunctional Sulfur-Containing Polymer Derivatives

[0126] Terminal-modified difunctional sulfur-containing polymers provided by the present disclosure and precursors thereof may be prepared by a number of methods known to those skilled in the art, including those described in the Examples herein. For example, to obtain terminal-modified difunctional sulfur-containing polymers of Formula (II), a difunctional sulfur-containing polymer of Formula (I) may be reacted with a compound having appropriate terminal groups.

[0127] For example, to obtain a vinyl-terminated sulfur-containing polymer of Formula (II), a sulfur-containing polymer of Formula (I) may be reacted with a compound containing a terminal vinyl group and an isocyanate group such as a group derived from TMI, 2-isocyanatoethyl methacrylate, or allyl isocyanate, in the presence of dibutyltin dilaurate catalyst at 76°C. As a further example, a sulfur-containing polymer of Formula (I) may be reacted with an alkene-ol such as 3-butene-1-ol and an aldehyde such as formaldehyde in the presence of a sulfonic acid (*e.g.*, 4.7 meq/g H^+) such as AMBERLYST™ 15 in an organic solvent such as toluene to provide a vinyl-terminated sulfur-containing polymer of Formula (II).

[0128] Silyl-terminated sulfur-containing polymers of Formula (II) may be prepared, for example, by reacting a sulfur-containing polymer of Formula (I) with an isocyanatoalkyltrialkoxysilane such as a 3-isocyanatopropyltrimethoxysilane or 3-isocyanatopropyltriethoxysilane in the presence of dibutyltin dilaurate at a temperature of 76°C to provide the corresponding silyl-terminated sulfur-containing polymer of Formula (II).

[0129] Epoxy-terminated sulfur-containing polymers of Formula (II) may be prepared, for example, by reacting a sulfur-containing polymer of Formula (I) in the presence of a monoepoxide such as epichlorohydrin to provide the corresponding epoxy-terminated sulfur-containing polymer of Formula (II).

[0130] Amine-terminated sulfur-containing polymers of Formula (III) may be prepared, for example, by reacting a vinyl-terminated sulfur-containing polymer Formula (II)(d) with aniline, an amino-substituted aniline such as 4-(aminomethyl)aniline, or an alkylamine such as n-butylamine optionally in the presence of a catalyst such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in an organic solvent to provide the corresponding amine-terminated sulfur-containing polymer of Formula (III). Alternatively, amine-terminated sulfur-containing polymers of Formula (III) may be obtained by reacting an isocyanate-terminated sulfur-containing polymer of Formula (I) with a diamine such as 4-(aminomethyl)aniline to provide the corresponding amine-terminated sulfur-containing polymer of Formula (III). Amine-terminated sulfur-containing polymers of Formula (III) may also be obtained by reacting a sulfur-containing polymer of Formula (I) with an amino-substituted benzoate such as ethyl-4-aminobenzoate in the presence of Bu_2SnO or NaOMe at elevated temperature to provide the corresponding amine-terminated sulfur-containing polymer of Formula (I). Amine-terminated sulfur-containing polymers of Formula (III) may also be prepared by reacting a tosyl-ester of a sulfur-containing polymer of Formula (III) with an amine-containing compound such as aniline in an organic solvent at elevated temperature to provide the corresponding amine terminated sulfur-containing polymer of Formula (III).

[0131] Thiol-terminated sulfur-containing polymers of Formula (IV) may be prepared by reacting a vinyl-terminated sulfur-containing polymer of Formula (II) such as the 2-isocyanatoethyl methacrylate adduct or the allyl isocyanate adduct as disclosed herein with a dithiol such as DMDO. Thiol-terminated sulfur-containing polymers of Formula (IV) may also be prepared by reacting a tosyl-ester of a sulfur-containing polymer of Formula (I) with NaSH in the presence of $MeN(Bu)_3^+Cl^-$ in water to provide the corresponding thiol-terminated sulfur-containing polymer of Formula (IV). Alternatively, a tosyl-ester of a sulfur-containing polymer of Formula (I) may be reacted with thiourea in the presence of $MeN(Bu)_3^+Cl^-$ in water to provide the tosylate salt of the thiourea adduct, which may then be reacted in the presence of base at elevated temperature to provide the corresponding thiol-terminated sulfur-containing polymer of Formula (IV). Alternatively, to obtain thiol-terminated sulfur-containing polymers of Formula (IV), a sulfur-containing polymer of Formula (I) may first be reacted with a diisocyanate such as TDI in the presence of dibutyltin dilaurate at 75°C to 80°C to provide the corresponding isocyanate-terminated sulfur-containing polymer of Formula (IV). The isocyanate-terminated sulfur-containing polymer of Formula (IV) may then be reacted with a mercaptoalkanol such as 2-mercaptoethanol or 3-mercaptopropanol to provide the corresponding thiol-terminated sulfur-containing polymer of Formula (IV).

[0132] Isocyanate-terminated sulfur-containing polymers of Formula (II) may be prepared, for example, by reacting a sulfur-containing polymer of Formula (I) with a diisocyanate such as TDI, ISONATE™ 143L (polycarbodiimide-modified diphenylmethane diisocyanate), DESMODUR® N3400 (1,3-diazetidine-2,4-dione, 1,3-bis(6-isocyanatohexyl)-), DESMODUR® I (isophorone diisocyanate, IPDI), or DESMODUR® W ($H_{12}MDI$) optionally in the presence of a catalyst such as dibutyltin dilaurate at a temperature from 70°C to 80°C. Isocyanate-terminated sulfur-containing polymers may be used as intermediates in the synthesis of other terminal-modified sulfur-containing polymers such as certain amine-terminated and thiol-terminated sulfur-containing polymers provided by the present disclosure.

Properties of Terminal-Modified Difunctional Sulfur-Containing Polymers

[0133] In certain embodiments, terminal-modified difunctional sulfur-containing polymers provided by the present disclosure are liquid at room temperature. Moreover, in certain embodiments, the sulfur-containing polymers have a viscosity, at 100% solids, of no more than 500 poise, such as 10 to 300 poise or, in some cases, 100 to 200 poise, at a temperature of 25°C and a pressure of 760 mm Hg determined according to ASTM D-2849 §79-90 using a Brookfield CAP 2000 viscometer. In certain embodiments, the T_g (glass transition temperature) of sulfur-containing polymer provided by the present disclosure is not higher than -40°C, and in certain embodiments, is not higher than -50°C.

Uses

[0134] Terminal-modified difunctional sulfur-containing polymers provided by the present disclosure may be used in compositions, such as sealants, coatings, and/or electrical potting compositions that include one or more of the sulfur-containing polymers provided by the present disclosure. A sealant composition refers to a composition capable of producing a film that has the ability to resist operational conditions, such as moisture and temperature, and at least partially block the transmission of materials, such as water, fuel, and other liquid and gases. In certain embodiments, sealant compositions provided by the present disclosure are useful, *e.g.*, as aerospace sealants and as linings for fuel tanks.

[0135] In certain embodiments, compositions provided by the present disclosure comprise, in addition to a sulfur-containing polymer of Formula (II), Formula (III), Formula (IVa), Formula (IVb),or a reaction product of any one of the reactions disclosed herein, or a combination of any of the foregoing, one or more additional sulfur-containing polymers. A sulfur-containing polymer can be any polymer having at least one sulfur atom in the repeating unit, including polymeric thiols, polythiols, thioethers, polythioethers, polyformals, and polysulfides. A "thiol," as used herein, refers to a compound comprising a thiol or mercaptan group, that is, an "SH" group, either as the sole functional group or in combination with other functional groups, such as hydroxyl groups, as is the case with, for example, thioglycerols. A polythiol refers to such a compound having more than one SH group, such as a dithiol or higher functionality thiol. Such groups are typically terminal and/or pendant such that they have a active hydrogen that is reactive with other functional groups. As used herein, the term "polysulfide" refers to any compound that comprises a sulfur-sulfur linkage (–S–S–). A polythiol can comprise both a terminal and/or pendant sulfur (–SH) and a non-reactive sulfur atom (–S– or –S–S–). Thus, the term polythiol generally encompasses polythioethers and polysulfides. Examples of additional sulfur-containing polymers suitable in compositions provided by the present disclosure include, for example, those disclosed in U.S. Patent Nos. 6,172,179, 6,509,418, and 7,009,032. In certain embodiments, compositions provided by the present disclosure comprise a polythioether having the structure:

$$-R^1-[-S-(CH_2)_2-O-[-R^2-O-]_m-(CH_2)_2-S-R^1-]_n-$$

wherein R^1 is selected from a C_{2-6} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} cycloalkylalkanediyl, $-[(-CH_2-)_p-X-]_q-(-CH_2-)_r-$, and $-[(-CH_2-)_p-X-]_q-(-CH_2-)_r-$ in which at least one $-CH_2-$ unit is substituted with a methyl group; R^2 is selected from C_{2-6} alkanediyl, C_{6-8} cycloalkanediyl, C_{6-10} cycloalkylalkanediyl, and $-[(-CH_2-)_p-X-]_q-(-CH_2-)_r-$; X is selected from O, S, and $-NR^6-$, where R^6 is selected from hydrogen and methyl; m is an integer selected from 0 to 10; n is an integer selected from 1 to 60; p is an integer selected from 2 to 6; q is an integer selected from 1 to 5, and r is an integer selected from 2 to 10. Such polythioethers are described in U.S. Patent No. 6,172,179 at col. 2, line 29 to col. 4, line 34. The one or more additional sulfur-containing polymers may be difunctional or multifunctional, for example, having from 3 to 6 terminal groups, or a mixture thereof.

[0136] In certain embodiments, compositions provided by the present disclosure comprise from 10 wt% to 90 wt% of a sulfur-containing polymer provided by the present disclosure, from 20 wt% to 80 wt%, from 30 wt% to 70 wt%, and in certain embodiments from 40 wt% to 60 wt%, where wt% is based on the total weight of all non-volatile components of the composition (*i.e.*, the dry weight). In certain embodiments, compositions provided by the present disclosure comprise from 10 wt% to 90 wt% of a sulfur-containing polymer provided by the present disclosure, from 20 wt% to 90 wt%, from 30 wt% to 90 wt%, from 40 wt% to 90 wt%, from 50 wt% to 90 wt%, from 60 wt% to 90 wt%, from 70 wt% to 90 wt%, and in certain embodiments from 80 wt% to 90 wt%, where wt% is based on the total weight of all non-volatile components of the composition (*i.e.*, the dry weight).

[0137] Curing agents suitable in compositions provided by the present disclosure include compounds that are reactive with the terminal groups of the sulfur-containing polymer, such as compounds that are reactive with hydroxyl groups, vinyl groups, epoxy groups, thiol groups amine groups, or isocyanate groups.

[0138] Examples of suitable curing agents that are reactive with hydroxyl groups include diisocyanates and polyisocyanates, examples of which are disclosed herein.

[0139] Examples of suitable curing agents that are reactive with vinyl groups include dithiols and polythiols, examples of which are disclosed herein.

[0140] Silyl-terminated sulfur-containing polymers provided by the present disclosure hydrolyze in the presence of water inducing self polymerization *via* condensation. Other catalysts for use with silyl-terminated sulfur-containing polymers include organotitanium compounds such as tetraisopropoxy titanium, tetra-*tert*-butoxy titanium, titanium di(isopropoxy)bis(ethylacetoacetate), and titanium di(isopropoxy)bis(acetylacetoacetate); organic tin compounds dibutyltin dilaurate, dibutyltin bisacetylacetoacetate, and tin octylate; metal dicarboxylates such as lead dioctylate; organozirconium compounds such as zirconium tetraacetyl acetonate; and organoaluminium compounds such as aluminum triacetyl- acetonate. Specific examples include diisopropoxy bis(ethyl acetoacetonate)titanium, diisopropoxy bis(acetyl acetonate)titanium, and dibutoxy bis(methyl acetoacetonate)titanium. In can be appreciated that because the curing agent for silyl-terminated sulfur-containing polymers can be atmospheric moisture, it is not necessary to include a curing agent to a curable composition containing silyl-terminated sulfur-containing polymers. Therefore, compositions comprising silyl-terminated sulfur-containing polymers and a curing agent for the silyl group refer to atmospheric moisture.

[0141] Examples of suitable curing agents that are reactive with epoxy groups include amines such as diethylenetriamine (DTA), triethylenetetramine (TTA), tetraethylenepentamine (TEPA), dipropenediamine (DPDA), diethylaminopropylamine (DEAPA), N-aminoethylpiperazine (N-AEP), isophoronediamine (IPDA), m-xylenediamine, diaminodiphenylmethane (DDM), diaminodiphenylsulfone (DDS); aromatic amines, ketimine; polyamines; polyamides; phenolic resins; anhydrides such phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, benzophenone tetracarboxylic anhydride, ethylene glycol bistrimellitate, glycerol tristrimellitate, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, endomethylene tetrahydrophthalic anhydride; polymercaptans; polysulfides; ultraviolet curing agents such as diphenyliodinium hexafluorophosphate, triphenylsulfonium hexafluorophosphate; and other curing agents known to those skilled in the art.

[0142] Examples of suitable curing agents that are reactive with thiol groups include diepoxides.

[0143] Examples of suitable curing agents that are reactive with amine groups include polymeric polyisocyanates, non-limiting examples of which include polyisocyanates having backbone groups chosen from urethane groups (–NH–C(O)–O–), thiourethane groups (–NH–C(O)–S–), thiocarbamate groups (–NH–C(S)–O–), dithiourethane linkages (–NH–C(S)–S–), and combinations of any of the foregoing.

[0144] Examples of suitable curing agents that are reactive with isocyanate groups include diamines, polyamines, polythiols, and polyols, including those disclosed herein.

[0145] Compositions provided by the present disclosure may contain from 90% to 150% , from 95% to 125%, and in certain embodiments, from 95% to 105% of the stoichiometric amount, where the stoichiometric amount is the proportion of the number of reactive isocyanate groups to the number of groups reactive with the isocyanate groups.. For example, a composition containing the same number of isocyanate groups and amine groups prior to reaction will have a stoichiometric amount of isocyanate groups and amine groups.

[0146] Compositions provided by the present disclosure may contain one or more different types of filler. Suitable fillers include those commonly known in the art, including inorganic fillers, such as carbon black and calcium carbonate ($CaCO_3$), and lightweight fillers. Suitable lightweight fillers include, for example, those described in U.S. Patent No. 6,525,168. In certain embodiments, a composition includes 5 wt% to 60 wt% of the filler or combination of fillers, 10 wt% to 50 wt%, and in certain embodiments, from 20 wt% to 40 wt%, based on the total dry weight of the composition.

[0147] As can be appreciated, the sulfur-containing polymers, curing agents, and fillers employed in a composition, as well as any additives, may be selected so as to be compatible with each other.

[0148] Compositions provided by the present disclosure may include one or more colorants, thixotropic agents, accelerators, retardants, adhesion promoters, solvents, masking agents, or a combination of any of the foregoing.

[0149] As used herein, the term “colorant” means any substance that imparts color and/or other opacity and/or other visual effect to the composition. A colorant can be of any suitable form, such as discrete particles, dispersions, solutions, and/or flakes. A single colorant or a mixture of two or more colorants can be used in a composition.

[0150] Examples of colorants include pigments, dyes and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. A colorant may include, for example, a finely divided solid powder that is insoluble but wettable under the conditions of use. A colorant may be organic or inorganic and may be agglomerated or non-agglomerated. Colorants may be incorporated into a composition by use of a grind vehicle, such as an acrylic grind vehicle.

[0151] Examples of pigments and/or pigment compositions include carbazole dioxazine crude pigment, azo, monoazo, diazo, naphthol AS, salt type (flakes), benzimidazolone, isoindolinone, isoindoline, polycyclic phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole, thioindigo, anthraquinone, indanthrone, anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcarbonium, quinophthalone pigments, diketo pyrrolo pyrrole red (DPPBO red), titanium dioxide, carbon black, and combinations of any of the foregoing.

[0152] Examples of dyes include, but are not limited to, those that are solvent- and/or aqueous-based such as phthalo green or blue, iron oxide, bismuth vanadate, anthraquinone, perylene, and quinacridone.

[0153] Examples of tints include pigments dispersed in water-based or water-miscible carriers such as AQUA-CHEM 896 commercially available from Degussa, Inc., CHARISMA COLORANTS and MAXITONER INDUSTRIAL COLORANTS commercially available from Accurate Dispersions division of Eastman Chemical, Inc.

[0154] As noted above, a colorant may be in the form of a dispersion including, for example, a nanoparticle dispersion. Nanoparticle dispersions may include one or more highly dispersed nanoparticle colorants and/or colorant particles that produce a desired visible color and/or opacity and/or visual effect. Nanoparticle dispersions may include colorants such as pigments or dyes having a particle size of less than 150 nm, such as less than 70 nm, or less than 30 nm. Nanoparticles may be produced by milling stock organic or inorganic pigments with grinding media having a particle size of less than 0.5 mm. Examples of nanoparticle dispersions and methods for making them are disclosed in U.S. Patent No. 6,875,800. Nanoparticle dispersions may also be produced by crystallization, precipitation, gas phase condensation, and/or chemical attrition (*i.e.*, partial dissolution). To minimize re-agglomeration of nanoparticles within the coating, a dispersion of resin-coated nanoparticles may be used. As used herein, a “dispersion of resin-coated nanoparticles” refers to a continuous phase in which are dispersed discreet “composite microparticles” that comprise a nanoparticle and a resin coating on the nanoparticle. Examples of dispersions containing resin-coated nanoparticles and methods for making them are disclosed in U.S. Patent No. 7438,972.

[0155] Examples of special effect compositions that may be used in compositions provided by the present disclosure include pigments and/or compositions that produce one or more appearance effects such as reflectance, pearlescence, metallic sheen, phosphorescence, fluorescence, photochromism, photosensitivity, thermochromism, goniochromism, and/or color-change. Additional special effect compositions can provide other perceivable properties, such as opacity or texture. In certain embodiments, special effect compositions may produce a color shift, such that the color of a composition changes when the coating is viewed at different angles. Examples of color effect compositions are disclosed in U.S. Patent No. 6,894,086. Additional color effect compositions may include transparent coated mica and/or synthetic mica, coated silica, coated alumina, a transparent liquid crystal pigment, a liquid crystal coating, and/or any composition wherein interference results from a refractive index differential within the material and not because of the refractive index differential between the surface of the material and the air.

[0156] In general, a colorant may comprise from 1 wt% to 65 wt% of a composition, from 2 wt% to 50 wt%, such as from 3 wt% to 40 wt%, or from 5 wt% to 35 wt%, with weight percent based on the total dry weight of the composition.

[0157] Thixotropes, for example, silica, may be used in an amount from 0.1 wt% to 5 wt%, based on the total dry weight of the composition.

[0158] Cure catalysts known to the art, such as amines, may be present in an amount from 0.1 to 5 weight percent, based on the total weight of the composition. Examples of suitable catalysts include 1,4-diaza-bicyclo[2.2.2]octane (DABCO®, commercially available from Air Products, Chemical Additives Division, Allentown, Pa.) and DMP-30® (an accelerant composition including 2,4,6-tris(dimethylaminomethyl)phenol.

[0159] Retardants, such as stearic acid, may be used in an amount from 0.1 wt% to 5 wt% of a composition, based on the total dry weight of the composition. Adhesion promoters, may be present in amount from 0.1 wt% to 15 wt% of a composition, based on the total dry weight of the composition. Examples of adhesion promoters include phenolics, such as METHYLON phenolic resin available from

Occidental Chemicals, and organosilanes, such as epoxy, mercapto or amino functional silanes, such as SILQUEST® A-187 and SILQUEST® A-1100 available from Momentive Performance Materials. Masking agents, such as pine fragrance or other scents, which may be useful in masking any low level odor of the composition, may be present in an amount from 0.1 wt% to 1 wt%, based on the total dry weight of the composition.

[0160] In certain embodiments, compositions provided by the present disclosure may comprise a plasticizer that may facilitate the use of sulfur-containing polymers having a higher glass transition temperature, T_g, than would ordinarily be useful in an aerospace sealant. For example, use of a plasticizer may effectively reduce the T_g of a composition, and thereby increase the low-temperature flexibility of the cured polymerizable composition beyond that which would be expected on the basis of the T_g of the sulfur-containing polymers alone. Plasticizers suitable in certain embodiments of the compositions include, for example, phthalate esters, chlorinated paraffins, and hydrogenated terphenyls. A plasticizer or combination of plasticizers may constitute from 1 wt% to 40 wt% of a composition, or from 1 wt% to 10 wt% of a composition. In certain embodiments, a composition may comprise one or more organic solvents, such as isopropyl alcohol, in an amount, for example, from 0 wt% to 15 wt%, from 0 wt % to 10 wt%, or from 0 wt% to 5 wt%, based on the non-dry weight of the composition.

[0161] In certain embodiments, compositions provided by the present disclosure are substantially free or, in some cases, completely free, of any solvent, such as an organic solvent or an aqueous solvent, *i.e.*, water. Stated differently, in certain embodiments, compositions provided by the present disclosure are substantially 100% solids.

[0162] In certain embodiments, compositions, such as sealant compositions, may be provided as multi-pack compositions, such as two-pack compositions, wherein one package comprises one or more sulfur-containing polymers provided by the present disclosure and a second package comprises one or more curing agents for the one or more sulfur-containing polymers. Additives and/or other materials may be added to either package as desired or necessary. The two packages may be combined and mixed prior to use. In certain embodiments, the pot life of the mixed polythioether and curing agent is at least 30 minutes, at least 1 hour, at least 2 hours, and in certain embodiments, more than 2 hours, where pot life refers to the period of time the composition remains suitable for use as a sealant after mixing.

[0163] Compositions provided by the present disclosure may be applied to any of a variety of substrates. Examples of substrates to which a composition may be applied include titanium, stainless steel, and aluminum, which may be anodized, primed, organic-coated or chromate-coated; epoxy; urethane; graphite; fiberglass composite; KEVLAR®; acrylics; and polycarbonates.

[0164] Compositions provided by the present disclosure may be applied directly onto the surface of a substrate or over an underlayer by any suitable coating process known to those of ordinary skill in the art.

[0165] In certain embodiments, compositions provided by the present disclosure are fuel-resistant. As used herein, the term "fuel resistant" means that a composition, when applied to a substrate and cured, can provide a cured product, such as a sealant, that has a percent volume swell of not greater than 40%, in some cases not greater than 25%, in some cases not greater than 20%, in yet other cases not more than 10%, after immersion for one week at 140°F (60°C) and ambient pressure in Jet Reference Fluid (JRF) Type I according to methods similar to those described in ASTM D792 (American Society for Testing and Materials) or AMS 3269 (Aerospace Material Specification. Jet Reference Fluid JRF Type I, as employed for determination of fuel resistance, has the following composition (*see* AMS 2629, issued July 1, 1989, § 3.1.1 etc., available from SAE (Society of Automotive Engineers): toluene: 28 ± 1% by volume; cyclohexane (technical): 34 ± 1% by volume; isooctane: 38 ± 1% by volume; and tertiary dibutyl disulfide: 1 ± 0.005% by volume.

[0166] In certain embodiments, compositions provide a cured product, such as a sealant, exhibiting an elongation of at least 100% and a tensile strength of at least 400 psi when measured in accordance with the procedure described in AMS 3279, § 3.3.17.1, test procedure AS5127/1, § 7.7.

[0167] In certain embodiments, compositions provide a cured product, such as a sealant exhibits a lap shear strength of greater than 200 psi and in some cases at least 400 psi when measured according to the procedure described in SAE AS5127/1 paragraph 7.8.

[0168] In certain embodiments, a cured sealant comprising a sulfur-containing polymer provided by the present disclosure meets the requirements for aerospace sealants as set forth in AMS 3277.

[0169] Furthermore, methods are provided for sealing an aperture utilizing a composition provided by the present disclosure. These methods comprise, for example, applying a composition provided by the present disclosure to a surface to seal an aperture; and curing the composition. In certain embodiments, a composition may be cured under ambient conditions, where ambient conditions refers to a temperature from 20°C to 25°C. In certain embodiments, a composition may be cured under conditions encompassing a temperature from 0°C to 100°C and humidity from 0% RH to 100% RH. In certain embodiments, a composition may be cured at a higher temperature such as at least 30°C, at least 40°C, and in certain embodiments, at least 50°C. In certain embodiments, a composition may be cured at room temperature, *e.g.*, 25°C. In certain embodiments, a composition may be cured upon exposure to actinic radiation such as ultraviolet radiation. As will also be appreciated, the methods may be used to seal apertures on aerospace vehicles.

EXAMPLES

[0170] Embodiments provided by the present disclosure are further illustrated by reference to the following examples, which describe the synthesis, properties, and uses of certain sulfur-containing polymers. It will be apparent to those skilled in the art that many modifications, both to materials, and methods, may be practiced without departing from the scope of the disclosure.

Example 1

Sulfur-Containing Polymer Synthesis

[0171] Thiodiglycol (549.84 g), paraformaldehyde (95% purity) (150.40 g), dithiodiglycol (77.1 g), AMBERLYST® 15 (107.7 g, Dow Chemical Company), and toluene (1,000 mL) were charged in a 2-liter, 4-neck, round-bottom flask. The flask was equipped with a heating mantle, thermocouple, temperature controller, and a Dean-Stark adapter fitted with a reflux condenser, dropping funnel, and inlet for nitrogen positive pressure. The reactants were stirred under a nitrogen atmosphere, heated to 118°C, and maintained at 118°C for about 9 h. During this period, collected water was periodically removed from the Dean-Stark adapter. The reaction mixture was then cooled to room temperature and filtered with suction through a coarse-fritted Buchner funnel (600 mL volume) with a 9.0 cm-diameter Whatman GF/A filter paper over the frit. The flask and filter cake were washed with 500 mL toluene. A filtrate was obtained. The filtrate was dried *in vacuo* using a 2-L, round bottomed flask (rotary evaporator, 7 torr final vacuum, 90°C water bath). A yellow, viscous polymer (529.8 g) was obtained. The sulfur-containing polymer had a hydroxyl number of 15.8 and a viscosity of 386 poise.

Example 2

Sulfur-Containing Polymer Synthesis

[0172] Thiodiglycol (1,832.79 g), paraformaldehyde (95% purity) (360.4 g), AMBERLYST® 15 (319.1 g, Dow Chemical Company), and toluene (1,000 mL) were charged in a 5-liter 4-neck round-bottom flask. The flask was equipped with a heating mantle, thermocouple, temperature controller, and a Dean-Stark adapter fitted with a reflux condenser, dropping funnel, and inlet for nitrogen positive pressure. The reactants were stirred under a nitrogen atmosphere, heated to 118°C, and maintained at 118°C for about 7 h. During this period, collected water was periodically removed from the Dean-Stark adapter. The reaction mixture was then cooled to room temperature and filtered with suction through a coarse-fritted Buchner funnel (600 mL volume) with a 9.0 cm-diameter Whatman GF/A filter paper over the frit. The flask and filter cake were washed with 500 mL toluene. A filtrate was obtained. The filtrate was dried *in vacuo* using a 2-L, round bottomed flask (rotary evaporator, 7 torr final vacuum, 90°C water bath). A yellow, viscous polymer (1,455.8 g) was obtained. The sulfur-containing polymer had a hydroxyl number of 34.5 and a viscosity of 92 poise.

Example 3

Acrylate-Terminated Sulfur-Containing Polymer

[0173] The sulfur-containing polymer of Example 2 (164.3 g) was charged into a 500-mL, 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer (PTFE paddle and bearing). The polymer was stirred at *ca.* 200 rpm and heated to 76.6°C (170°F), followed by the addition of isocyanatoethyl methacrylate (10.1 g) and a 0.01% solution of dibutyltin dilaurate dissolved in methyl ethyl ketone (1.7 g). The reaction mixture was maintained at 76.6°C for 5 h and then cooled to room temperature. A 1% solution of benzoyl chloride dissolved in methyl ethyl ketone (1.8 g) was then added to the reaction mixture. The resulting polymer had a viscosity of 177 poise.

Example 4

Allyl-Terminated Sulfur-Containing Polymer

[0174] The sulfur-containing polymer in Example 2 (143.1 g) was charged into a 500-mL, 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer (PTFE paddle and bearing). The polymer was stirred at *ca.* 200 rpm and heated to 76.6°C (170°F), followed by the addition of allyl isocyanate (4.8 g) and a 0.01% solution of dibutyltin dilaurate dissolved in methyl ethyl ketone (1.5 g). The reaction mixture was maintained at 76.6°C for 5 h and then cooled to room temperature. The resulting polymer had a viscosity of 176 poise.

Example 5

TMI-Terminated Sulfur-Containing Polymer

[0175] The sulfur-containing polymer in Example 2 (150.9 g) was charged into a 500-mL, 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer (PTFE paddle and bearing). The polymer was stirred at *ca.* 200 rpm and heated to 76.6°C (170°F), followed by the addition of 3-isopropenyl-α, α-dimethylbenzyl isocyanate (12.7 g, available from Cytec Industries) and a 0.01% solution of dibutyltin dilaurate dissolved in methyl ethyl ketone (1.63 g). The reaction mixture was maintained at 76.6°C for 6 hours and then cooled to room temperature. The resulting polymer had a viscosity of 291 poise.

Example 6

Curing of Acrylate-Terminated Sulfur-Containing Polymer

[0176] The curing reaction was carried out in a 100 g plastic container equipped with a lid. The acrylate-terminated sulfur-containing polymer of Example 3 (40.8 g) and Irgacure® 2022 (0.2 g, 0.5% by weight, BASF) were mixed by hand in the container. The container was then placed in a speed mixer (DAC 600 FVZ) and mixed for 1 min at 2,300 rpm. The polymer was poured over a circular (5 in-diameter) metal lid (pre-treated with Valspar Mold Release 225), and placed under ultraviolet (UV) radiation for 15 sec, after which time the polymer had completely cured. A Super Six curing unit (Fusion Systems Inc.) was used to provide the UV radiation. The curing unit was equipped with a 300 W H-bulb, which produced UV wavelengths ranging from 200 nm to 450 nm. A total dosage of 3.103 J/cm^2 UV energy, measured using a UV power puck (EIT, Inc., Sterling, VA) was applied to the polymer composition. Up to 2 inches of cured polymer was obtained. The hardness of the polymer was measured with a durometer to be 32 Shore A. Hardness data was obtained according to ASTM D 2240.

Example 7

Curing of TMI-Terminated Sulfur-Containing Polymer

[0177] The curing reaction was performed in a 100 g plastic container equipped with a lid. The TMI-terminated sulfur-containing polymer described in Example 5 (40.8 g) and IRGACURE® 2022 (0.2 g, 0.5% by weight) were mixed by hand in the container. The container was then placed in a speed mixer (DAC 600 FVZ) and mixed for 1 min at 2,300 rpm. The polymer was poured over a circular (5 inch-diameter) metal lid (pre-treated with Valspar Mold Release 225), and placed under UV light for 15 sec. A Super Six curing unit (Fusion Systems Inc.) was used to provide the UV radiation. The curing unit was equipped with a 300 W H-bulb, which produced UV wavelengths ranging from 200 nm to 450 nm. A total dosage of 3.103 J/cm^2 UV energy, measured using a UV power puck (EIT, Inc., Sterling, VA) was applied to the polymer composition. Up to 2 mm of cured polymer was obtained.

Example 8

Silyl-terminated Sulfur-Containing Polymer

[0178] The sulfur-containing polymer of Example 2 (151.5 g) was charged into a 500-mL, 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, and an inlet for nitrogen positive pressure, mechanical stirrer (PTFE paddle and bearing). The polymer was stirred at *ca.* 200 rpm and heated to 76.6°C (170°F), followed by the addition of SILQUEST®A-Link 25 (23.1 g, Momentive Performance Materials) and a 0.01% solution of dibutyltin dilaurate dissolved in methyl ethyl ketone (2.8 g). The reaction mixture was maintained at 76.6°C for 5 h and then cooled to room temperature. The resulting polymer had a viscosity of 80 poise.

Example 9

Silyl-Terminated Sulfur-Containing Polymer

[0179] The sulfur-containing polymer of Example 2 (162.3 g) was charged into a 500-mL, 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer (PTFE paddle and bearing). The polymer was stirred at *ca.* 200 rpm and heated to 76.6°C (170°F), followed by the addition of SILQUEST® A-Link 35 (20.6 g, Momentive Performance Materials) and a 0.01% solution of dibutyltin dilaurate dissolved in methyl ethyl ketone (1.8 g). The reaction mixture was maintained at 76.6°C for 5 h and then cooled to room temperature. A 1% solution of benzoyl chloride dissolved in methyl ethyl ketone (1.8 g) was then added to the reaction mixture. The resulting polymer had a viscosity of 114 poise.

Example 10

Sealant Composition: Silyl-Terminated Sulfur-Containing Polymer

[0180] A sealant composition was prepared by mixing the silyl-terminated sulfur-containing polymer described in Example 8 and other ingredients described in Table 1.

Table 1. Sealant Composition

Component	Charge Weight, grams
Polymer from Example 8	35
Carbon Black	15
Plasticizer[1]	2
Metacure T-12[2]	0.5

[1] Available from Solvay.

[2] Available from Air Products and Chemicals, Inc.

[0181] After mixing, the composition was sealed in a moisture-free container and allowed to stand in the moisture-free container for approximately one month at ambient conditions. After storing for one month, the container was opened exposing the polymer to the ambient environment to cure the polymer. Hardness measurements were taken periodically using a Rex Durometer according to ASTM D2240. In addition, cured samples were immersed in Jet Reference Fuel (JRF) Type I for 7 days at 140°F. After immersion, volume swell percentage and percent weight loss of the cured sample were measured according to SAE AS5127/1 section 7.4. The results are presented in Tables 2 and 3.

Table 2. Curing Time vs. Hardness

Cure Time	**Hardness, Shore A**
60 days	70

Table 3. Volume Swell and Weight Loss After JRF Immersion

Sealant Composition	**Average Volume Swell, %**	**Average Weight Loss, %**
Example 10/Table 1	8.14	2.13

Example 11

Sealant Composition: Silyl-Terminated Sulfur-Containing Polymer

[0182] A sealant composition was prepared by mixing the silyl-terminated sulfur-containing polymer described in Example 9 and other ingredients described in Table 4.

Table 4. Sealant Composition

Component	**Charge Weight, grams**
Polymer from Example 9	35
Carbon Black	15
Plasticizer	2
Metacure T-12	0.5

[0183] After mixing, the composition was then sealed in a moisture-free container and allowed to stand in moisture-free conditions for approximately one month at ambient conditions. After one month of storage, the container was opened the polymer exposed to the ambient environment (room temperature and humidity) to cure the polymer. Hardness measurements were taken periodically using a Rex Durometer according to ASTM D2240. In addition, cured samples were immersed in Jet Reference Fuel (JRF) Type I for 7 days at 140°F. After immersion, volume swell percentage and percent weight loss of a cured sample were measured according to SAE AS5127/1 section 7.4. The results are presented in Tables 5 and 6.

Table 5. Curing Time vs. Hardness

Cure Time	**Hardness, Shore A**
48 hr	25
3 days	43
4 days	49
30 days	63

Table 6. Volume Swell and Weight Loss After JRF Immersion

Sealant Composition	**Average Volume Swell, %**	**Average Weight Loss, %**
Table 4	8.43	1.86

Example 12

Thiol-Terminated Sulfur-Containing Polymer

[0184] Dimercaptodioxaoctane (2.0 g, dissolved in 40 mL toluene) and 1,8-diazabicyclo-[5,4,0]undec-7-ene (DBU) (0.03 g, available from Air Products and Chemicals) were charged into a 300-mL 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer (PTFE paddle and bearing). The mixture was stirred at *ca.* 200 rpm and the acrylate-terminated sulfur-containing polymer of Example 3 (54.6 g, dissolved in 40 ml toluene) was added drop-wise to the flask. The reaction mixture was heated to 100°C and maintained at 100°C for 10 h. Toluene was then removed from the reaction mixture under vacuum. The resulting polymer had a mercaptan equivalent weight of 5,129 and a viscosity of 201 poise.

Example 13

Thiol-Terminated Sulfur-Containing Polymer

[0185] Dimercaptodioxaoctane (4.06 g), the acrylate-terminated sulfur-containing polymer of Example 3 (93.6 g), and VAZO®-67 (1.1 g, available from Dupont) were charged into a 500-mL, 4-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer (PTFE paddle and bearing). The mixture was stirred at *ca.* 200 rpm and heated to 80°C and maintained at 80°C for 15 h. Additional VAZO®-67 (1.0 g) was charged to the reaction mixture during the reaction. The resulting polymer had a mercaptan equivalent weight of 4,834 and a viscosity of 299 poise.

Example 14

Performance Data for Thiol-Terminated Sulfur-Containing Polymer of Example 12

[0186] The curing reaction was performed in a 100 g plastic container equipped with a lid. The thiol-terminated sulfur-containing polymer described in Example 13 (51.3 g), diethylene glycol divinyl ether (7.91 g), and IRGACURE® 2022 (0.30 g, 0.5% by weight) were mixed by hand in the container. The container was then placed in a speed mixer (DAC 600 FVZ) and mixed for 1 min at 2,300 rpm. The polymer was poured over a circular (5 inch-diameter) metal lid (pre-treated with Valspar Mold Release 225), and placed under UV light for 15 sec, after which time the polymer had completely cured. A Super Six curing unit (Fusion Systems Inc.) was used to provide the UV radiation. The curing unit was equipped with a 300 W H-bulb, which produced UV wavelengths ranging from 200 nm to 450 nm. A total dosage of 3.103 J/cm^2 UV energy, measured using a UV power puck (EIT, Inc., Sterling, VA) was applied to the polymer composition.

Example 15

Sulfur-Containing Polymer Reaction with Methyl Mercaptoacetate

[0187] The sulfur-containing polymer of Example 2 (89.6 g), methyl mercaptoacetate (21.4 g) and sodium methoxide (0.4 g) were charged into a 300-mL, 3-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, mechanical stirrer (PTFE paddle and bearing), and a Dean-Stark trap connected to a reflux condenser and topped with an inlet for nitrogen positive pressure. The mixture was heated to 150°C and stirred at 300 rpm. The mixture was maintained at 150°C for 48 h. The solvent was removed at 150°C under vacuum for 1.4 h. The resulting polymer had a viscosity of 41 poise and a mercaptan equivalent weight of 6,934.

Example 16

Sulfur-Containing Polymer Reaction with Mercaptoacetic Acid

[0188] The sulfur-containing polymer of Example 2(89.6 g), mercaptoacetic acid (13.8 g), hafnium chloride-THF complex ($HfCl_4 \cdot 2THF$, 1.20 g, available from Aldrich) and toluene (75 mL) were charged into a 300-mL, 3-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, mechanical stirrer (PTFE paddle and bearing), and a Dean-Stark trap connected to a reflux condenser and topped with inlet for nitrogen positive pressure. The mixture was heated to 130°C and stirred at 300 rpm. The mixture was maintained at 130°C for 18 h. $NaHCO_3$ (12.8 g) was then added to the reaction mixture to consume excess mercaptoacetic acid while stirring briefly for 4 min. The product was filtered through a Buchner funnel with Whatman GF/A paper (7.0 cm dia.) and thoroughly washed with 100 mL toluene. The resulting filtrate was stripped *in vacuo* (rotary evaporator, 90°C water bath, < 5 torr final vacuum) to afford 90.1 g of a viscous polymer having a viscosity of 52 poise and a mercaptan equivalent weight of 4,223.

Example 17

Polyformal Polymer Reaction with TDI and Mercaptopropanol

[0189] The sulfur-containing polymer of Example 2 (89.6 g) and toluene diisocyanate (17.5 g) were charged into a 300-mL, 3-neck round-bottom flask. The flask was equipped with a mantle, thermocouple, temperature controller, mechanical stirrer (PTFE paddle and bearing), and a nitrogen inlet. The mixture was heated to

71°C and stirred at 200 rpm and maintained at 71°C for 27 h. 3-Mercaptopropanol (7.9 g) was then added and the reaction mixture was heated to 77°C and stirred at 200 rpm for 41 h. Finally, the reaction mixture was heated to 100°C under vacuum for 30 min to remove unreacted 3-mercaptopropanol. The resulting polymer had a mercaptan equivalent weight of 2,630.

Example 18

Epoxy Terminated Sulfur-Containing Polymer

[0190] Sodium hydride 60% dispersion in mineral oil (Aldrich) (1.92 g) was charged to a 4-neck round bottom flask equipped with a heating mantle, thermocouple, temperature controller, an inlet for nitrogen positive pressure, and a mechanical stirrer, and blanketed with nitrogen. The dispersion was washed three times with 5 mL heptanes. The reaction was stirred at room temperature, followed by the addition of a premixed solution of sulfur-containing polymer of Example 2 (157.08 g) and dry dimethylsulfoxide (312 g) over 45 minutes. The reaction was stirred at *ca.* 200 rpm for 4 hours and epichlorohydrin (11.10 g) (Aldrich) was added dropwise while the reaction was allowed to exotherm to 50°C. The reaction was held for 2 hours at 50°C, cooled to room temperature, and stirred overnight. The solution was then poured into 1,100 g of water and extracted twice with methylene chloride, washed with a saturated aqueous solution of NaCl, and dried over sodium sulfate. The solvent was removed under vacuum to provide a light brown oil with an epoxy equivalent wt of 1,960 g/meq.

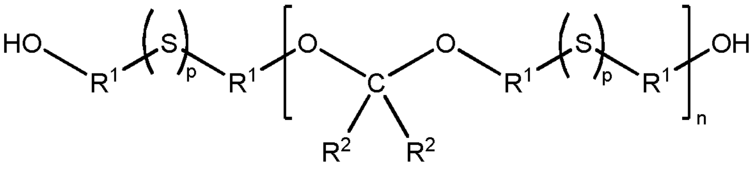
[0191] Finally, it should be noted that there are alternative ways of implementing the embodiments disclosed herein. Accordingly, the present embodiments are to be considered as illustrative and not restrictive. Furthermore, the claims are not to be limited to the details given herein, and are entitled their full scope and equivalents thereof.

CLAIMS

What is claimed is:

1. A terminal-modified sulfur-containing polymer comprising the reaction products of reactants comprising:

(a) a sulfur-containing polymer of Formula (I):



(I)

wherein:

n is an integer selected from 1 to 50;

each p is independently selected from 1 and 2;

each R^1 is independently selected from C_{2-6} alkanediyl; and

each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and

(b) a compound comprising a terminal group selected from a vinyl group, a silyl group, an amine group, and an epoxy group; and a group that is reactive with the terminal hydroxyl groups of the polymer of Formula (I).

2. The terminal-modified sulfur-containing polymer of claim 1, wherein the sulfur-containing polymer of Formula (I) comprises the reaction products of:

(i) a sulfur-containing diol; and

(ii) a reactant selected from an aldehyde, ketone, and a combination thereof.

3. The terminal-modified sulfur-containing polymer of claim 2, wherein the sulfur-containing diol is selected from 2,2'-thiodiethanol, 3,3'-thiobis(propan-1-ol), 4,4'-thiobis(butan-1-ol), and a combination of any of the foregoing.

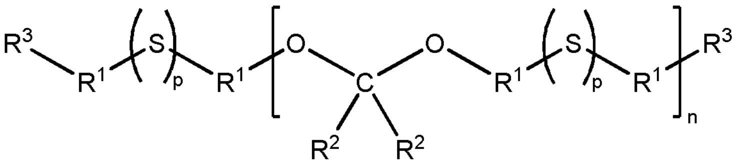
4. The terminal-modified sulfur-containing polymer of claim 2, wherein (ii) is an aldehyde and comprises formaldehyde.

5. The terminal-modified sulfur-containing polymer of claim 1, wherein the sulfur-containing polymer of Formula (I) has a hydroxyl number from 10 to 100.

6. The terminal-modified sulfur-containing polymer of claim 1, wherein each R^1 is the same and is selected from ethane-1,2-diyl and propane-1,3-diyl; and each R^2 is independently selected from hydrogen, methyl, and ethyl.

7. The terminal-modified sulfur-containing polymer of claim 1, wherein n is an integer selected from 7 to 30.

8. A terminal-modified sulfur-containing polymer of Formula (II):



(II)

wherein:

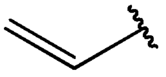
n is an integer selected from 1 to 50;

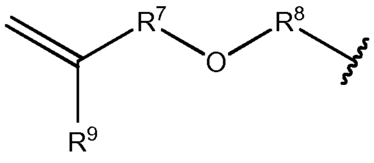
each p is independently selected from 1 and 2;

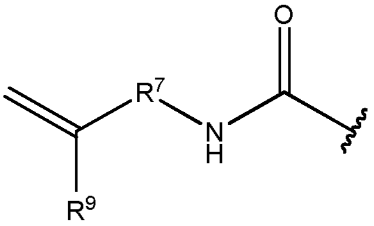
each R^1 is independently selected from C_{2-6} alkanediyl;

each R^2 is independently selected from hydrogen, C_{1-6} alkyl, C_{7-12} phenylalkyl, substituted C_{7-12} phenylalkyl, C_{6-12} cycloalkylalkyl, substituted C_{6-12} cycloalkylalkyl, C_{3-12} cycloalkyl, substituted C_{3-12} cycloalkyl, C_{6-12} aryl, and substituted C_{6-12} aryl; and each R^3 is $-OR^{3'}$ wherein $R^{3'}$ is selected from a vinyl-terminated group, a silyl-terminated group, an amine-terminated group, an epoxy-terminated group, and a thiol-terminated group.

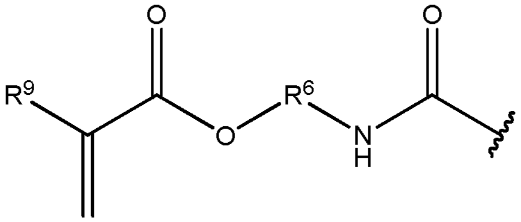
9. The terminal-modified sulfur-containing polymer of claim 8, wherein each R^3 is a vinyl-terminated group and is independently selected from a group of Formula (a), Formula (b), Formula (c), Formula (d), and Formula (e):





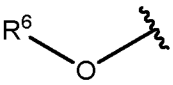


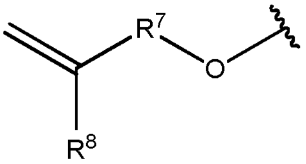
(a) (b) (c)

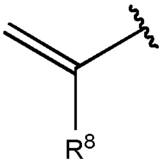


(d)

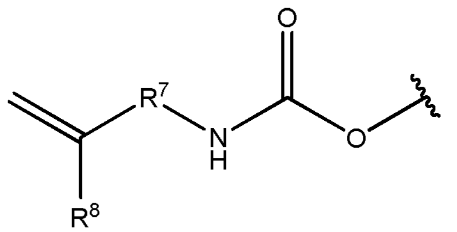
wherein:



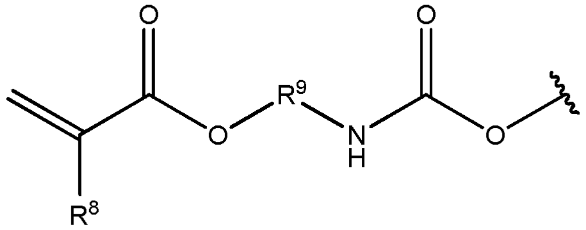




(a) (b) (c)



and



(d) (e)

wherein:

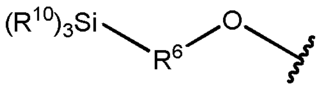
each R^6 is a moiety derived from an ethylenically unsaturated monoisocyanate;

each R^7 is selected from C_{2-6} alkanediyl and C_{2-6} heteroalkanediyl;

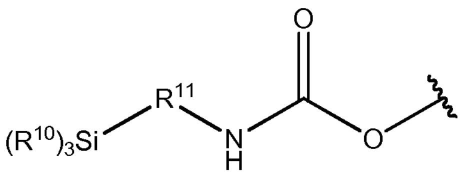
each R^8 is selected from hydrogen, C_{1-6} alkyl, and phenyl; and

each R^9 is selected from C_{2-6} alkanediyl, C_{2-6} heteroalkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{6-12} heteroarenediyl, substituted C_{6-12} heteroarenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{3-12} heterocycloalkanediyl, substituted C_{3-12} heterocycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} heteroalkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

10. The terminal-modified sulfur-containing polymer of claim 8, wherein each R^3 is a silyl-terminated group and is a group of Formula (f) and Formula (g):



and



(f) (g)

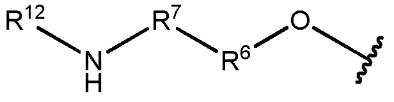
wherein:

each R^6 is derived from an ethylenically unsaturated monoisocyanate;

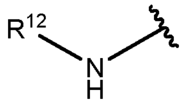
each R^{10} is independently selected from C_{1-6} alkyl, C_{1-6} alkoxy, C_{5-6} cycloalkyl, C_{6-12} cycloalkylalkyl, phenyl, and C_{7-12} phenylalkyl; wherein at least one R^{10} is C_{1-6} alkoxy; and

each R^{11} is C_{1-6} alkanediyl.

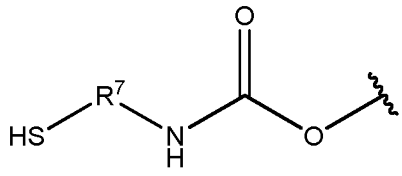
11. The terminal-modified sulfur-containing polymer of claim 8, wherein each R^3 is an amine-terminated group and is independently selected from a group of Formula (h), Formula (i), Formula (j), Formula (k), Formula (l), and Formula (m):



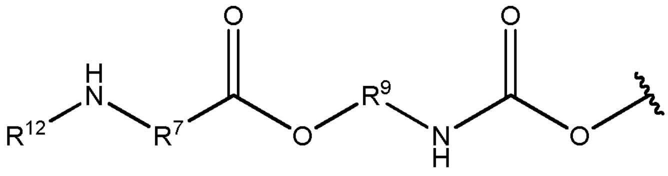
(h)



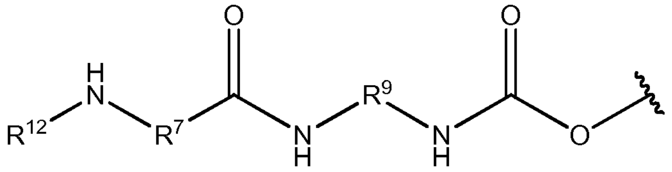
(i)



(j)

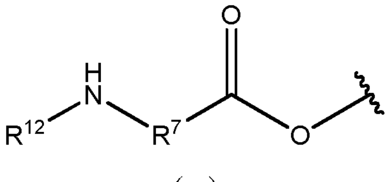


(k)



and

(l)



(m)

wherein:

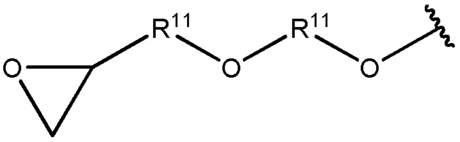
each R^6 is selected from a group derived from a diisocyanate and a group derived from an ethylenically unsaturated monoisocyanate;

each R^7 is selected from a bond and C_{2-6} alkanediyl;

each R^9 is selected from C_{2-6} alkanediyl, C_{2-6} heteroalkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{6-12} heteroarenediyl, substituted C_{6-12} heteroarenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{3-12} heterocycloalkanediyl, substituted C_{3-12} heterocycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} heteroalkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl; and

each R^{12} is selected from hydrogen, C_{1-6} alkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} alkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

12. The terminal-modified sulfur-containing polymer of claim 8, wherein each R^3 is an epoxy-terminated group and is a group of Formula (n):

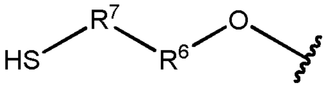


(n)

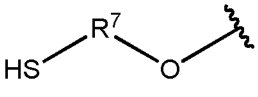
wherein:

each R^{11} is independently C_{1-6} alkanediyl.

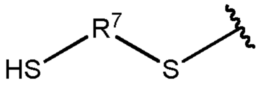
13. The terminal-modified sulfur-containing polymer of claim 8, wherein each R^3 is a thiol-terminated group and is independently selected from a group of Formula (o), Formula (p), Formula (q), Formula (r), Formula (s), Formula (t), Formula (u), and Formula (v):



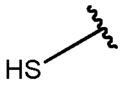
(o)

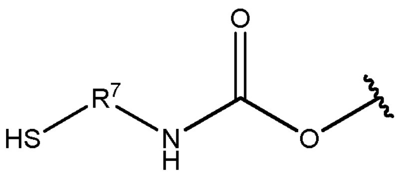


(p)

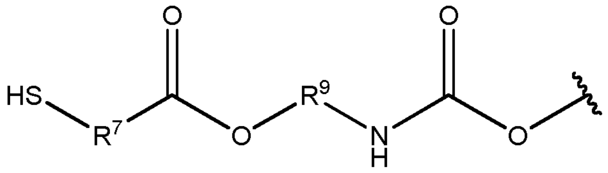


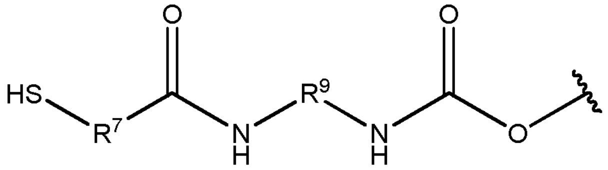
(q)





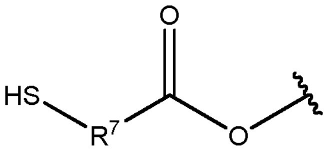
(r) (s)





(t) (u)

and



(v)

wherein:

each R^6 is selected from a moiety derived from a diisocyanate and a moiety derived from an ethylenically unsaturated monoisocyanate;

each R^7 is selected from C_{2-14} alkanediyl and C_{2-14} heteroalkanediyl; and

each R^9 is selected from C_{2-6} alkanediyl, C_{2-6} heteroalkanediyl, C_{6-12} arenediyl, substituted C_{6-12} arenediyl, C_{6-12} heteroarenediyl, substituted C_{6-12} heteroarenediyl, C_{3-12} cycloalkanediyl, substituted C_{3-12} cycloalkanediyl, C_{3-12} heterocycloalkanediyl, substituted C_{3-12} heterocycloalkanediyl, C_{7-18} alkanearenediyl, substituted C_{7-18} heteroalkanearenediyl, C_{4-18} alkanecycloalkanediyl, and substituted C_{4-18} alkanecycloalkanediyl.

14. A composition comprising the terminal-modified sulfur-containing polymer of claim 1; and a curing agent that is reactive with the terminal-modified sulfur-containing polymer.

15. An aperture sealed with a sealant comprising the composition of claim 14.

16. A composition comprising the terminal-modified sulfur-containing polymer of claim 8; and a curing agent that is reactive with the terminal-modified sulfur-containing polymer.

17. An aperture sealed with a sealant comprising the composition of claim 16.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/029436

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G75/12 C09D181/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/199603 A1 (COSMAN MICHAEL A [US]) 21 August 2008 (2008-08-21) cited in the application the whole document -----	1-17
A	US 3 997 612 A (LENKE GERD M ET AL) 14 December 1976 (1976-12-14) the whole document -----	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 14 June 2012	Date of mailing of the international search report 25/06/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Jung, Andreas

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/029436

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008199603 A1	21-08-2008	US 2008199603 A1	21-08-2008
		US 2008199694 A1	21-08-2008
		US 2008200610 A1	21-08-2008
		US 2010003525 A1	07-01-2010
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