

GLYCIDYL (METH)ACRYLATE MATERIAL AND METHODS OF USE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims the benefit of U.S. Provisional Patent Application No. 63/546,966, filed November 2, 2023, which is incorporated by reference.

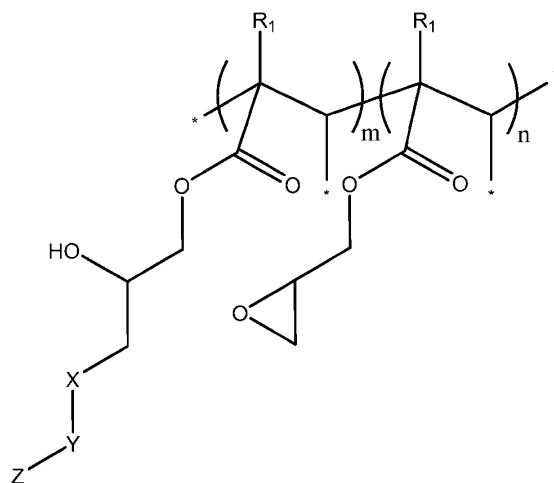
BACKGROUND OF THE INVENTION

[0002] Membrane-based liquid treatment processes have been utilized in a number of industries. For example, the direct flow filtration (DFF) and tangential flow filtration (TFF), including micro-, ultra-, nano-filtration and diafiltration, can be used for separation of dissolved molecules or suspended particulates.

[0003] However, removing small soluble particulates, such as metal ions, from aqueous and/or organic solutions remains a challenge. Thus, there remains a need for materials and methods for removing one or more metal ions from a solution. The invention provides such materials and methods. These and other advantages (e.g., simple and clean conjugation, uniform conjugation, rotational mobility of ligand, efficient deprotonation, and/or accessible chelation/coordination of the ligand) of the invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

BRIEF SUMMARY OF THE INVENTION

[0004] The invention provides a material comprising a glycidyl (meth)acrylate of Formula (I):



Formula (I),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R₁ independently is hydrogen or methyl, each X independently is -O-, -COO-, -S-, piperazinyl, or -NR₂-, R₂ is hydrogen, aryl, heteroaryl, C₁₋₆ alkyl aryl, C₁₋₆ alkyl heteroaryl, or C₁₋₆ alkyl, each Y independently is optionally present and is -NR₃- or optionally substituted C₁₋₆ alkyl, R₃ is hydrogen or C₁₋₆ alkyl, each Z independently is aryl (e.g., halogenated aryl), heteroaryl, or C₂₋₆ heterocyclyl, each of which is optionally substituted, and each * independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one * is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp³-sp³ carbon-carbon bond.

[0005] The invention further provides a method of making a material described herein, the method comprising (i) (a) irradiating (e.g., radiating) a polymeric support with an irradiation (e.g., a radiation) source and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof or (b) generating radicals on a polymeric support in the presence of glycidyl (meth)acrylate or a polymer thereof, wherein the polymeric support comprises one or more C-H aliphatic bonds, to graft the glycidyl (meth)acrylate or a polymer thereof on the polymeric support via one or more sp³-sp³ carbon-carbon bonds, and (ii) modifying the grafted glycidyl (meth)acrylate or a polymer thereof with one or more compounds of formula X'-Y'-Z', wherein X' is HO-, HOOC-, HS-, piperazinyl, or HNR₂-, R₂ is hydrogen, aryl, heteroaryl, C₁₋₆ alkyl aryl, C₁₋₆ alkyl heteroaryl, or C₁₋₆ alkyl, Y' is optionally present and is -NR₃- or optionally substituted C₁₋₆

alkyl, R₃ is hydrogen or C₁₋₆ alkyl, and Z' is aryl (e.g., halogenated aryl), heteroaryl, or C₂₋₆ heterocyclyl, each of which is optionally substituted.

[0006] The invention further provides a method of removing one or more metal ions from a solution comprising passing the solution through a material described herein or contacting the solution with the material described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1A provides a scanning electron microscope (SEM) image of a top surface of the 3-picolyamine modified glycidyl methacrylate grafted high density polyethylene (HDPE) prepared in Example 1.

[0008] FIG. 1B provides a scanning electron microscope (SEM) image of a cross-section of the 3-picolyamine modified glycidyl methacrylate grafted HDPE prepared in Example 1.

[0009] FIG. 2 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from cyclohexanone (CHN) solvent exhibited by the 3-picolyamine modified glycidyl methacrylate grafted HDPE prepared in Example 2, as described in Example 3.

[0010] FIG. 3 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether (PGME) solvent exhibited by the 3-picolyamine modified glycidyl methacrylate grafted HDPE prepared in Example 2, as described in Example 3.

[0011] FIG. 4 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) solvent exhibited by the 3-picolyamine modified glycidyl methacrylate grafted HDPE prepared in Example 2, as described in Example 3.

[0012] FIG. 5 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from cyclohexanone (CHN) solvent exhibited by the 4-fluorobenzylamine-modified glycidyl (meth)acrylate grafted HDPE prepared in Example 4, as described in Example 5.

[0013] FIG. 6 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether (PGME) solvent exhibited by the 4-fluorobenzylamine-modified glycidyl (meth)acrylate grafted HDPE prepared in Example 4, as described in Example 5.

[0014] FIG. 7 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) solvent exhibited by the 4-fluorobenzylamine-modified glycidyl (meth)acrylate grafted HDPE prepared in Example 4, as described in Example 5.

[0015] FIG. 8A provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from cyclohexanone (CHN) solvent exhibited by the composite material with an orientation of one layer of the HDPE coated material of Example 2 on top and one layer of the HDPE coated material of Example 4 on bottom, as described in Example 6.

[0016] FIG. 8B provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from cyclohexanone (CHN) solvent exhibited by the composite material with an orientation of one layer of the HDPE coated material of Example 4 on top and one layer of the HDPE coated material of Example 2 on bottom, as described in Example 6.

[0017] FIG. 9A provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether (PGME) solvent exhibited by the composite material with an orientation of one layer of the HDPE coated material of Example 2 on top and one layer of the HDPE coated material of Example 4 on bottom, as described in Example 6.

[0018] FIG. 9B provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether (PGME) solvent exhibited by the composite material with an orientation of one layer of the HDPE coated material of Example 4 on top and one layer of the HDPE coated material of Example 2 on bottom, as described in Example 6.

[0019] FIG. 10A provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) solvent exhibited by the composite material with an orientation of one layer of the HDPE coated material of Example 2 on top and one layer of the HDPE coated material of Example 4 on bottom, as described in Example 6.

[0020] FIG. 10B provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) solvent exhibited by the composite material with an orientation of one layer of the HDPE coated material of Example 4 on top and one layer of the HDPE coated material of Example 2 on bottom, as described in Example 6.

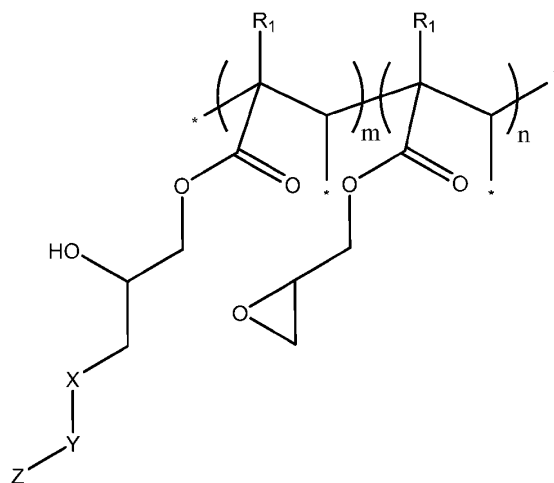
[0021] FIG. 11 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from cyclohexanone (CHN) solvent exhibited by the 3-picolylamine- and 4-fluorobenzylamine-modified glycidyl (meth)acrylate grafted HDPE prepared in Example 7, as described in Example 8.

[0022] FIG. 12 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether (PGME) solvent exhibited by the 3-picolylamine- and 4-fluorobenzylamine-modified glycidyl (meth)acrylate grafted HDPE prepared in Example 7, as described in Example 8.

[0023] FIG. 13 provides a bar graph showing the metal removal efficiency (MRE) percentage of removing titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver ions from propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) solvent exhibited by the 3-picolylamine- and 4-fluorobenzylamine-modified glycidyl (meth)acrylate grafted HDPE prepared in Example 7, as described in Example 8.

DETAILED DESCRIPTION OF THE INVENTION

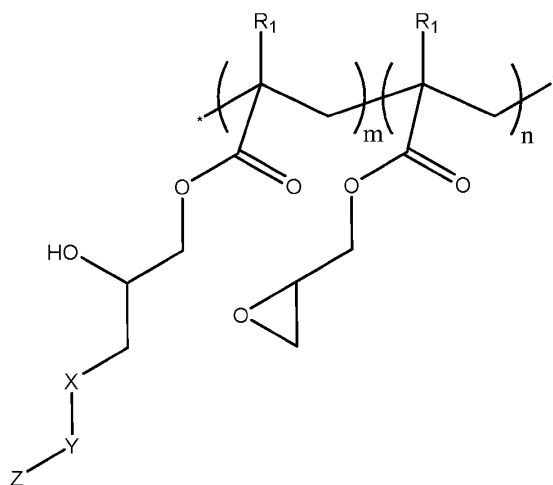
[0024] An aspect of the invention provides a material comprising a glycidyl (meth)acrylate of Formula (I):



Formula (I),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R₁ independently is hydrogen or methyl, each X independently is -O-, -COO-, -S-, piperazinyl, or -NR₂-, R₂ is hydrogen, aryl, heteroaryl, C₁₋₆ alkyl aryl, C₁₋₆ alkyl heteroaryl, or C₁₋₆ alkyl, each Y independently is optionally present and is -NR₃- or optionally substituted C₁₋₆ alkyl, R₃ is hydrogen or C₁₋₆ alkyl, each Z independently is aryl (e.g., halogenated aryl), heteroaryl, or C₂₋₆ heterocyclyl, each of which is optionally substituted, and each * independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one * is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp³-sp³ carbon-carbon bond.

[0025] In some embodiments, the material comprises a glycidyl (meth)acrylate of Formula (Ia):



Formula (Ia),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R_1 independently is hydrogen or methyl, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl, R_3 is hydrogen or C_{1-6} alkyl, each Z independently is aryl (e.g., halogenated aryl), heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted, and each $*$ independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one $*$ is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp^3 - sp^3 carbon-carbon bond.

[0026] As used herein, the term “(meth)acrylate” refers to an acrylate or a methacrylate. Thus, in any of the embodiments of the material described herein, each R_1 independently is hydrogen or methyl. In some embodiments, each R_1 is methyl. In other embodiments, each R_1 is hydrogen.

[0027] In any of the embodiments of the material, described herein, m is an integer from 1 to 10000 (e.g., 1 to 5000, 1 to 1000, 1 to 500, 1 to 100, 10 to 50, or 1 to 10). In some embodiments, m is an integer from 1 to 1000. In certain embodiments, m is 1, i.e., glycidyl (meth)acrylate monomer is grafted on the remainder of the material. In other embodiments, m is greater than 1, i.e., glycidyl (meth)acrylate polymer is grafted on the remainder of the material.

[0028] In any of the embodiments of the material, described herein, n is an integer from 0 to 10000 (e.g., 0 to 5000, 0 to 1000, 0 to 500, 0 to 100, 0 to 50, or 0 to 10). In other words, the unmodified glycidyl (meth)acrylate monomer, designated with variable n, is optionally present. In some embodiments, n is an integer from 0 to 1000. In certain embodiments, the unmodified glycidyl (meth)acrylate monomer is present such that n is an integer from 1 to 10000 (e.g., 1 to 5000, 1 to 1000, 1 to 500, 1 to 100, 10 to 50, or 1 to 10). In some embodiments, n is an integer from 1 to 1000.

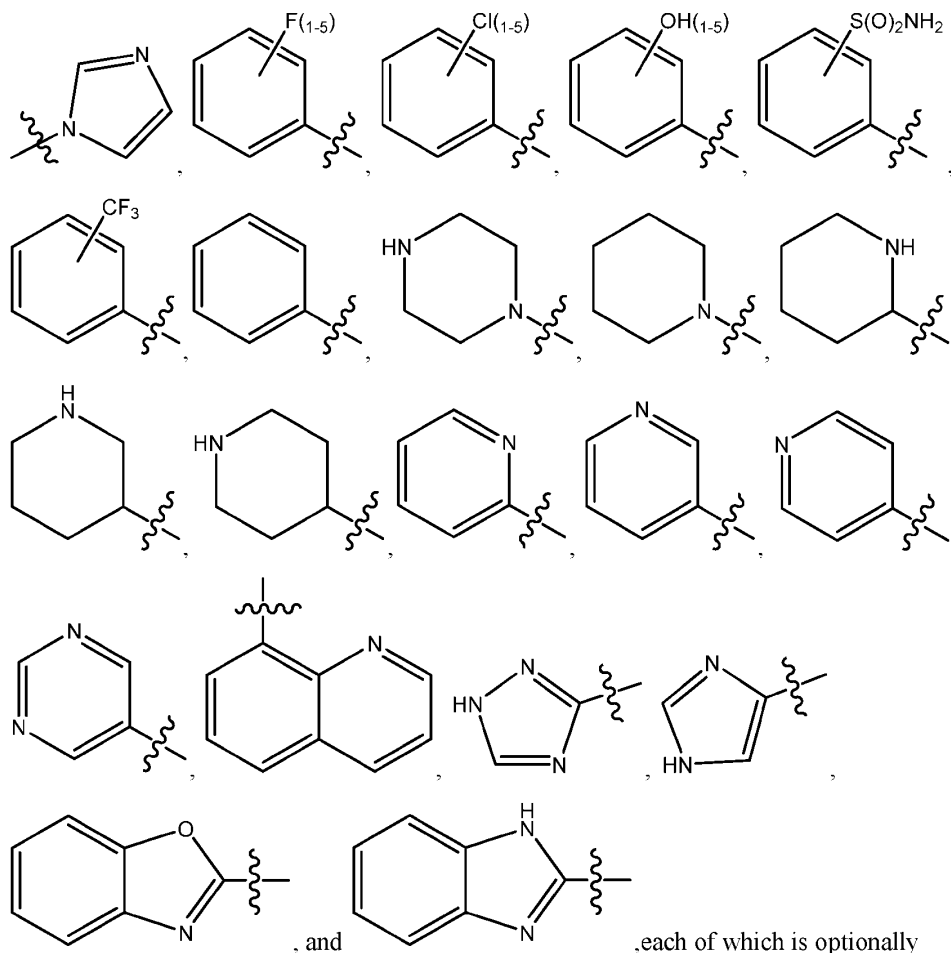
[0029] In any of the embodiments of the material, described herein, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, wherein R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl). In some embodiments, each X independently is $-NR_2-$ and R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl). In some embodiments, each X is $-S-$.

[0030] In any of the embodiments of the material, described herein, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl), wherein R_3 is hydrogen or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl). In some embodiments, each Y independently is $-NR_3-$, wherein R_3 is hydrogen or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl). In other embodiments, each Y independently is optionally substituted C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl).

[0031] In any of the embodiments of the material, described herein, each Z independently is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted. For example, Z can be phenyl, furyl, benzofuranyl, thiophenyl, benzothiophenyl, pyrrolyl, indolyl, isoindolyl, azaindolyl, pyridyl, quinoliny, isoquinoliny, oxazolyl, isooxazolyl, benzoxazolyl, pyrazolyl, imidazolyl, benzimidazolyl, thiazolyl, benzothiazolyl, isothiazolyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, cinnoliny, phthalazinyl, quinazolinyl, morpholinyl, pyrrolidinonyl, pyrrolidinyl, piperidinyl, hydantoinyl, valerolactamyl, oxiranyl, oxetanyl, tetrahydrofuranyl, tetrahydropyranyl, tetrahydropyridinyl, tetrahydroprimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, tetrahydropyrimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, piperazinyl, or dihydropyrimidinyl, each of which is optionally substituted. In some embodiments, at least one Z is a halogenated aryl (e.g., fluorinated aryl)

or halogenated heteroaryl (e.g., fluorinated heteroaryl). Alternatively, or additionally, at least one Z is optionally substituted pyridyl. In certain embodiments, at least one Z is optionally substituted pyridyl.

[0032] In some embodiments, each Z independently is selected from the following:

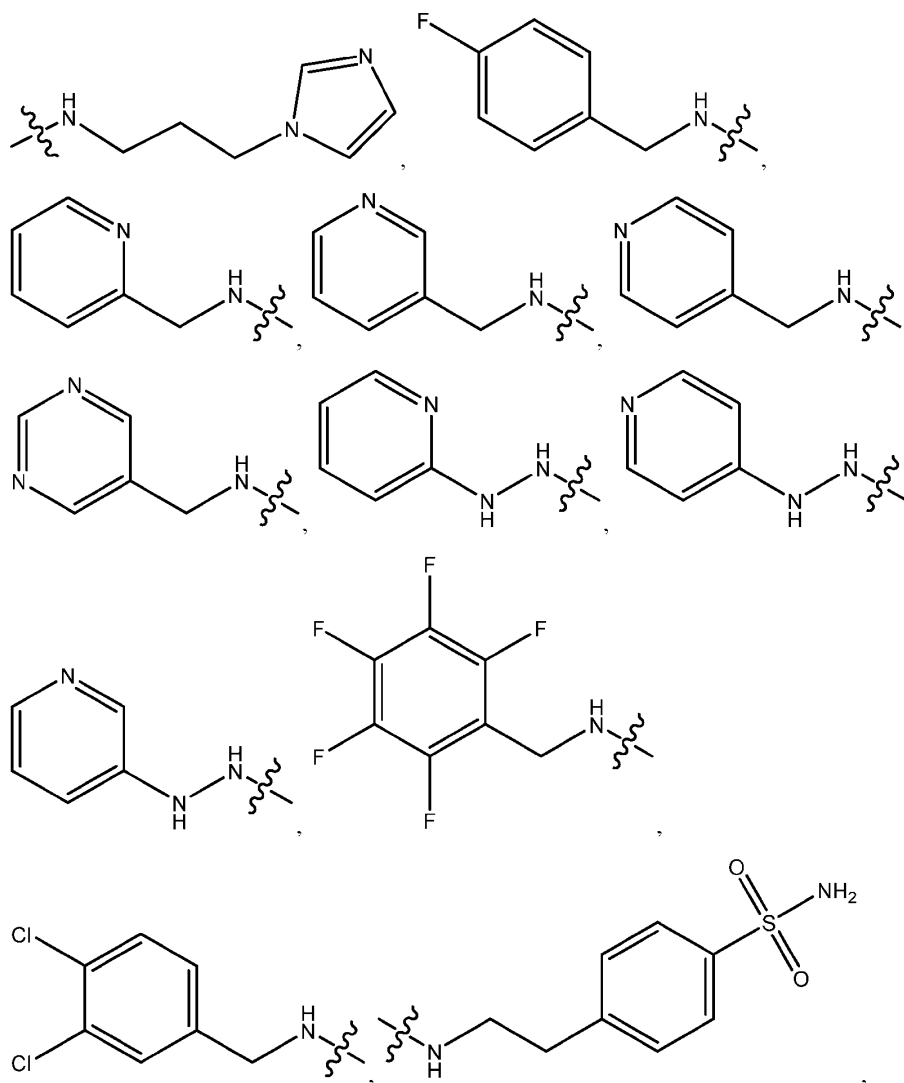


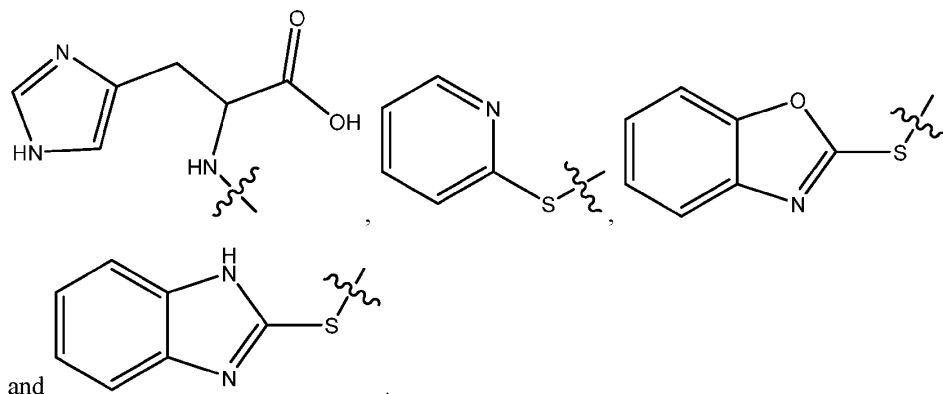
substituted.

[0033] As used herein, the term “optionally substituted” refers to one or more optional substituents selected from halo (e.g., fluoro, chloro, bromo, or iodo), cyano, nitro, trifluoromethyl, sulfo (e.g., sulfates, sulfonates, sulfoxides, etc.), hydroxyl, amino (e.g., a primary, secondary, or tertiary amine having 1 to 8 carbons), C_{1-8} alkyl, C_{1-8} alkoxy, C_{1-8} aminoalkyl, C_{1-8} hydroxyalkyl, and any combination thereof. Alternatively, or additionally,

when referring to an optionally substituted aryl, heteroaryl, or C₂₋₆ heterocyclyl, the term “optionally substituted” can refer to a fused or bridged aryl, heteroaryl, or C₂₋₆ heterocyclyl.

[0034] In some embodiments, each moiety X-Y-Z independently is selected from the following:





[0035] In any of the embodiments of the material described herein, each * independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one * is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp³-sp³ carbon-carbon bond. As used herein, the term “a terminating group” refers to any chemical moiety remaining as a result of quenching a free radical.

Common terminating groups will be readily apparent to a person of ordinary skill in the art.

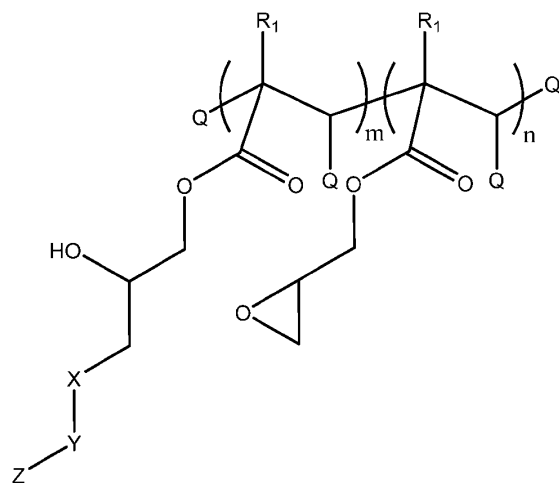
In some of the embodiments of the material described herein, each * independently represents hydrogen or a bond to a remainder of the material, provided that at least one * is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp³-sp³ carbon-carbon bond. In some embodiments, the material comprising a glycidyl (meth)acrylate of Formula (I) or a glycidyl (meth)acrylate of Formula (Ia) has more than one C-C bond with the remainder of the material. Alternatively, or additionally, the material can comprise more than one glycidyl (meth)acrylate of Formula (I) or glycidyl (meth)acrylate of Formula (Ia).

[0036] The glycidyl (meth)acrylate of Formula (I) or glycidyl (meth)acrylate of Formula (Ia) can be incorporated into any suitable material (e.g., chemical compound or media) so long as the glycidyl (meth)acrylate of Formula (I) or glycidyl (meth)acrylate of Formula (Ia) is bound to the remainder of the material via at least one carbon designated with an * in Formulae (I) and (Ia), wherein the remainder of the material is bound via a sp³-sp³ carbon-carbon bond. It will be readily understood to a person of ordinary skill in the art that the glycidyl (meth)acrylate of Formula (I) or glycidyl (meth)acrylate of Formula (Ia) can be incorporated into the material any number of times at any number of locations. Thus, the material can be any suitable material (e.g., chemical compound or media) comprising an

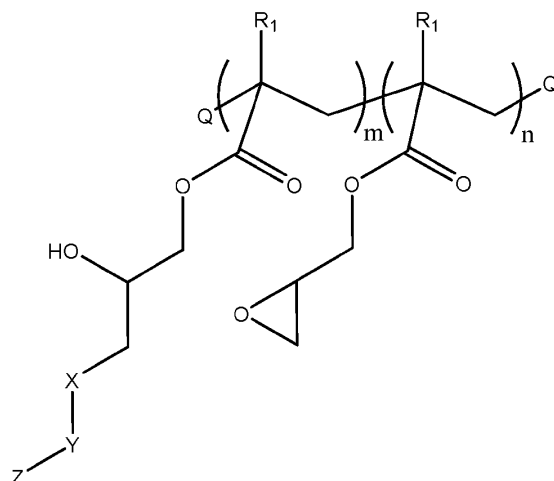
aliphatic C-H bond available for a sp^3-sp^3 carbon-carbon bond. In some embodiments, the material is porous such that a liquid or fluid can be passed through the material.

[0037] In some embodiments, the remainder of the material to which the glycidyl (meth)acrylate of Formula (I) or glycidyl (meth)acrylate of Formula (Ia) is bound is a macromolecular support selected from a membrane (e.g., a porous membrane or a permeable membrane), a fibrous media, a polymeric coating (e.g., a laminate or sealant such as a polyurethane coating, an epoxy coating, an acrylic coating, etc.) or material (e.g., gelatin, alginate, starch, polyethylene, polypropylene, nylon, polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, polyethylene/polypropylene oxide, polyacrylonitrile, poly(meth)acrylate, poly(meth)acrylamide, polyamide, polyimide, polyester, cellulose, polystyrene, etc.), a metal organic framework, a monolith support (e.g., a catalyst support), a bead (e.g., a polymeric bead), a filter, or a resin (e.g., a chromatographic resin). In some embodiments, the macromolecular support comprises gelatin, alginate, starch, polyethylene (e.g., high density polyethylene), polypropylene, nylon, polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, polyethylene/polypropylene oxide, polyacrylonitrile, poly(meth)acrylate, poly(meth)acrylamide, polyamide (e.g., nylon), polyimide, polyester, cellulose, polystyrene, or a combination thereof. In certain embodiments, the macromolecular support comprises polyethylene, polypropylene, nylon, polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, polyethylene/polypropylene oxide, polyacrylonitrile, cellulose, or a combination thereof. In preferred embodiments, the macromolecular support comprises polyvinylidene fluoride, polyethylene (e.g., high density polyethylene), polypropylene, nylon, or a combination thereof.

[0038] Thus, in some embodiments, the material is of formula (II):



or formula (IIa):



or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R_1 independently is hydrogen or methyl, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl, R_3 is hydrogen or C_{1-6} alkyl, each Z independently is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted, and each Q independently is hydrogen, a terminating group, or MS, provided that at least one Q is MS, and each MS independently is a macromolecular support selected from a membrane, a fibrous media, a

polymeric coating or material, a metal organic framework, a monolith support, a bead, a filter, or a resin, and wherein MS is bound via an sp³-sp³ carbon-carbon bond. All other definitions and embodiments, with respect to variables m, n, R₁, X, Y, Z, and the macromolecular support are as described herein with respect to the inventive material.

[0039] In any of the embodiments of the material described herein, each Q independently is hydrogen, a terminating group, or MS, provided that at least one Q is MS, wherein MS is bound via an sp³-sp³ carbon-carbon bond. In some embodiments of the material described herein, each Q independently is hydrogen or MS, provided that at least one Q is MS, wherein MS is bound via an sp³-sp³ carbon-carbon bond. In certain embodiments, the material of formula (II) or formula (IIa) has more than one C-MS bond.

[0040] In some embodiments, the material comprises a 3-picolylamine-modified glycidyl (meth)acrylate, a 4-fluorobenzylamine-modified glycidyl (meth)acrylate, a 2-picolylamine-modified glycidyl (meth)acrylate, a 1-(3-aminopropyl) imidazole-modified glycidyl (meth)acrylate, or a combination thereof. In that respect, the material disclosed herein can comprise one or more -X-Y-Z moieties, as defined herein. For example, the material can comprise a 3-picolylamine-modified glycidyl (meth)acrylate, a 4-fluorobenzylamine-modified glycidyl (meth)acrylate, a 2-picolylamine-modified glycidyl (meth)acrylate, or a 1-(3-aminopropyl) imidazole-modified glycidyl (meth)acrylate, or the material can comprise any combination of these modifications. In some embodiments, the material comprises a combination of 3-picolylamine-modified glycidyl (meth)acrylate and 4-fluorobenzylamine-modified glycidyl (meth)acrylate.

[0041] In some embodiments the material described herein exists as a film (e.g., a thin film). The film can have any suitable thickness. For example, the film can have a thickness of about 2 mil to about 20 mil, about 2 mil to about 15 mil, about 2 mil to about 10 mil, about 5 mil to about 20 mil, about 5 mil to about 15 mil, about 5 mil to about 10 mil, about 7 mil to about 20 mil, about 7 mil to about 15 mil, or about 7 mil to about 10 mil. Alternatively, or additionally, the material described herein can comprise multiple films (e.g., thin films) that are stacked to form a composite material (e.g., a composite film). Thus, in some embodiments, the material described herein is layered (e.g., stacked) to provide a composite material comprising one or more layers of the material described herein. Thus, each of the layers of the composite material can comprise a material of formula (I) or (Ia) or formula (II) or (IIa) comprising one or more X-Y-Z moieties. In some embodiments, the one or more X-

Y-Z moieties of each layer is the same. In other embodiments, the one or more X-Y-Z moieties of each layer is different.

[0042] The invention also provides an aspect of a method of making a material described herein, the method comprising:

(i) (a) irradiating (e.g., radiating) a polymeric support with an irradiation (e.g., a radiation) source and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof or (b) generating radicals on a polymeric support in the presence of glycidyl (meth)acrylate or a polymer thereof, wherein the polymeric support comprises one or more C-H aliphatic bonds, to graft the glycidyl (meth)acrylate or a polymer thereof on the polymeric support via one or more sp³-sp³ carbon-carbon bonds, and

(ii) modifying the grafted glycidyl (meth)acrylate or a polymer thereof with one or more compounds of formula X'-Y'-Z', wherein X' is HO-, HOOC-, HS-, piperazinyl, or HNR₂-, R₂ is hydrogen, aryl, heteroaryl, C₁₋₆ alkyl aryl, C₁₋₆ alkyl heteroaryl, or C₁₋₆ alkyl, Y' is optionally present and is -NR₃- or optionally substituted C₁₋₆ alkyl, R₃ is hydrogen or C₁₋₆ alkyl, and Z' is aryl, heteroaryl, or C₂₋₆ heterocyclyl, each of which is optionally substituted. All other definitions and embodiments, with respect to variables m, n, R₁, X, Y, Z, and the macromolecular support are as described herein with respect to the inventive material. In some embodiments, step (i) is performed in an oxygen-free environment (e.g., less than 50 ppm O₂, less than 40 ppm O₂, less than 30 ppm O₂, less than 20 ppm O₂, less than 10 ppm O₂, or less than 5 ppm O₂). In some embodiments, step (ii) is performed in an oxygen-free environment (e.g., less than 50 ppm O₂, less than 40 ppm O₂, less than 30 ppm O₂, less than 20 ppm O₂, less than 10 ppm O₂, or less than 5 ppm O₂). In certain embodiments, steps (i) and (ii) are performed in an oxygen-free environment (e.g., less than 50 ppm O₂, less than 40 ppm O₂, less than 30 ppm O₂, less than 20 ppm O₂, or less than 10 ppm O₂). In certain embodiments, step (i) and/or step (ii) is performed in an oxygen in an oxygen free environment having from 0 to 10 ppm O₂, 0 to 5 ppm O₂, 2 to 10 ppm O₂, or from 2 to 5 ppm O₂.

[0043] The method comprises (a) irradiating (e.g., radiating) a polymeric support with an irradiation (e.g., a radiation) source and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof or (b) generating radicals on a polymeric support in the presence of glycidyl (meth)acrylate or a polymer thereof, wherein the polymeric support comprises one or more C-H aliphatic bonds, to graft the glycidyl (meth)acrylate or a polymer thereof on the polymeric support via one or more sp³-sp³

carbon-carbon bonds. Thus, the polymeric support can be irradiated or activated (e.g., by generating radicals) in the presence or absence of the glycidyl (meth)acrylate or a polymer thereof. If the polymeric support is irradiated or activated (e.g., by generating radicals) in the absence of the glycidyl (meth)acrylate or a polymer thereof, the glycidyl (meth)acrylate or a polymer thereof can be subsequently impregnated on the polymeric support.

[0044] The polymeric support can be irradiated or activated (e.g., by generating radicals) by any suitable means. For example, the polymeric support can be irradiated or activated (e.g., by generating radicals) with E-beam irradiation, gamma irradiation, X-ray irradiation, UV light, plasma, corona discharge, a chemical initiator, or a combination thereof. In some embodiments, the method comprises irradiating the polymeric support with E-beam irradiation, gamma irradiation, X-ray irradiation, or a combination thereof and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof. In other embodiments, the method comprises generating radicals on the polymeric support with UV light, plasma, corona discharge, a chemical initiator, or a combination thereof in the presence of glycidyl (meth)acrylate or a polymer thereof.

[0045] The glycidyl (meth)acrylate or a polymer thereof can be grafted on the polymeric support using any suitable means at any suitable temperature. For example, the irradiated or activated (e.g., by generating radicals) polymeric support can be dipped in a solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof, the irradiated or activated (e.g., by generating radicals) polymeric support can be spray coated with a solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof, or the polymeric support can be irradiated or activated (e.g., by generating radicals) while submersed in a solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof. The glycidyl (meth)acrylate or a polymer thereof can be grafted on the polymeric support at a temperature of 0 °C to 100 °C, 0 °C to 50 °C, 10 °C to 30 °C, or 20 °C to 30 °C. Typically, the glycidyl (meth)acrylate or a polymer thereof is grafted on the polymeric support at room temperature (e.g., approximately 25 °C). In some embodiments, the polymeric support or irradiated or activated (e.g., by generating radicals) polymeric support is in the form of a roll, which can be wound or unwound during any stage of the process.

[0046] The solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof can contain any suitable solvent. For example, the solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof can comprise an organic solvent such as, for example, alcohols (e.g., ethanol or methanol), sulfoxides, sulfides,

acetates, ethers, amides, nitriles, or a combination thereof. In some embodiments, the solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof comprises an alcohol such as, for example, methanol as a solvent. In certain embodiments, the solution (e.g., a monomer solution) containing glycidyl (meth)acrylate or a polymer thereof further comprises allyl glycidyl ether, 1,2-epoxy-5-hexene, 3,4-epoxy-1-butene, allyl 2,3-epoxypropyl ether, or a combination thereof.

[0047] The method comprises modifying the grafted glycidyl (meth)acrylate or a polymer thereof with one or more compounds of formula $X'-Y'-Z'$, wherein X' is $HO-$, $HOOC-$, $HS-$, piperazinyl, or HNR_2- , R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl), Y' is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl), R_3 is hydrogen or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl), and Z' is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted.

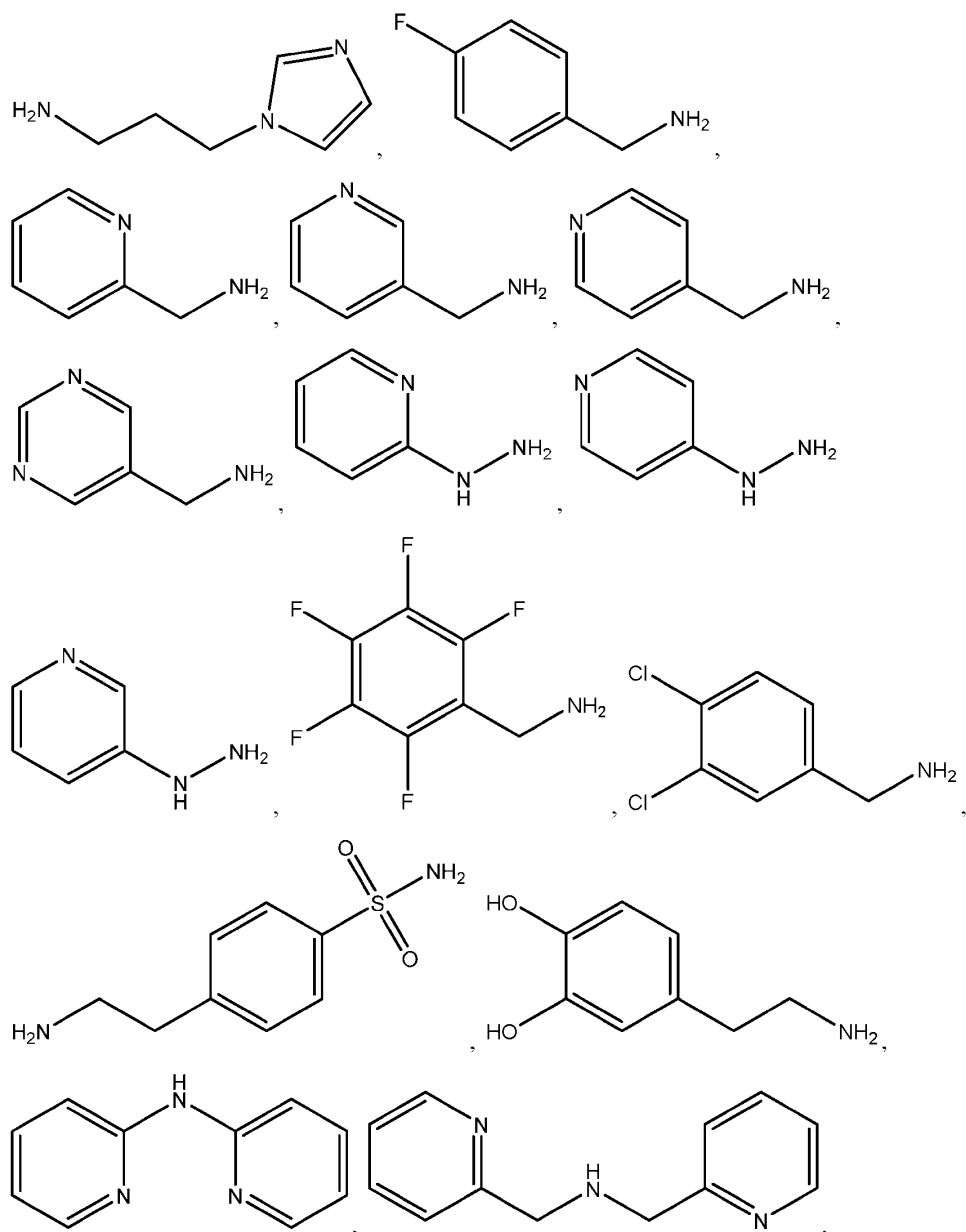
[0048] In some embodiments of the compound of formula $X'-Y'-Z'$, X' is $-NHR_2$ and R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl). In some embodiments of the compound of formula $X'-Y'-Z'$, X' is $-SH$.

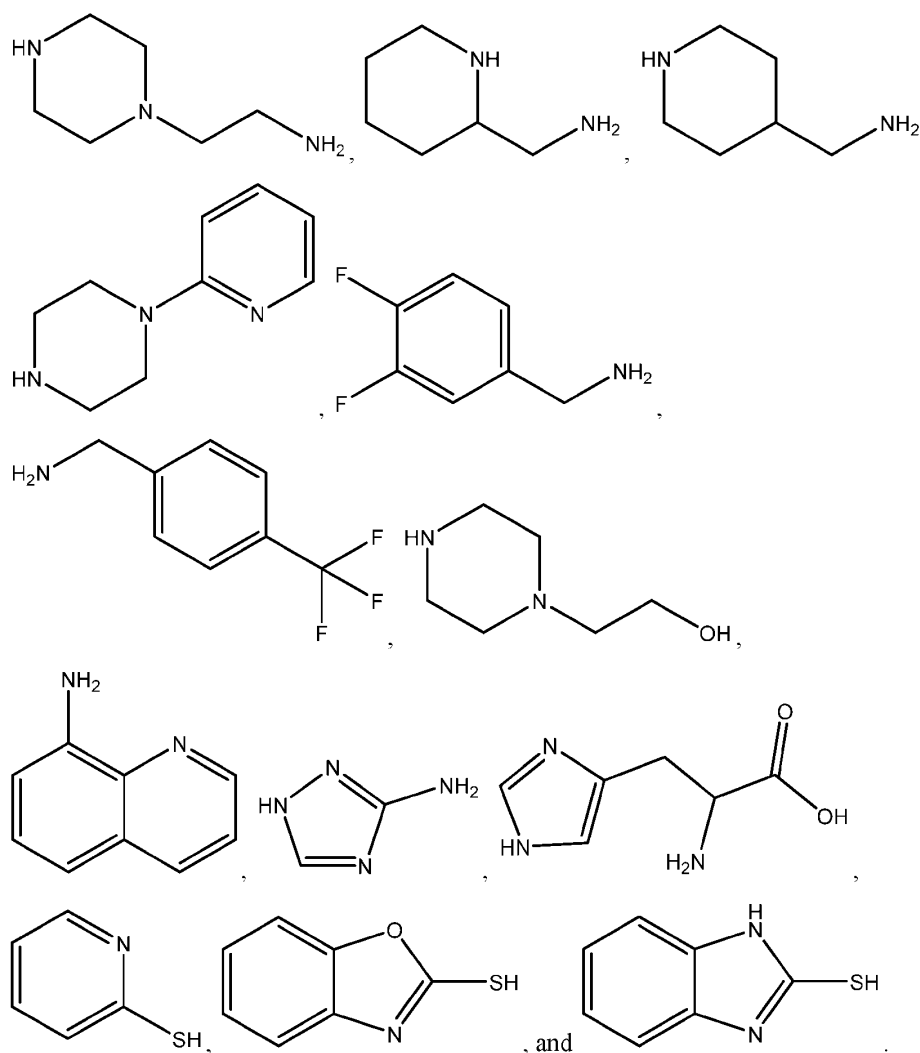
[0049] In some embodiments of the compound of formula $X'-Y'-Z'$, Y' is $-NR_3-$, wherein R_3 is hydrogen or C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl). In other embodiments of the compound of formula $X'-Y'-Z'$, Y' is optionally substituted C_{1-6} alkyl (e.g., straight chained or branched methyl, ethyl, propyl, butyl, pentyl, or hexyl).

[0050] In some embodiments of the compound of formula $X'-Y'-Z'$, Z' is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted. For example, Z can be phenyl, furyl, benzofuranyl, thiophenyl, benzothiophenyl, pyrrolyl, indolyl, isoindolyl, azaindolyl, pyridyl, quinoliny, isoquinoliny, oxazolyl, isooxazolyl, benzoxazolyl, pyrazolyl, imidazolyl, benzimidazolyl, thiazolyl, benzothiazolyl, isothiazolyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, cinnoliny, phthalazinyl, quinazolinyl, morpholiny, pyrrolidinonyl, pyrrolidinyl, piperidinyl, hydantoinyl, valerolactamyl, oxiranyl, oxetanyl, tetrahydrofuranyl, tetrahydropyranyl, tetrahydropyridinyl, tetrahydropyrimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, tetrahydropyrimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl,

piperazinyl, or dihydropyrimidinyl, each of which is optionally substituted. In some embodiments, Z' is a halogenated aryl (e.g., fluorinated aryl) or halogenated heteroaryl (e.g., fluorinated heteroaryl). In certain embodiments, Z' is optionally substituted pyridyl.

[0051] In some embodiments, the compound of formula $X'-Y'-Z'$ is selected from the following compounds:





[0052] The grafted glycidyl (meth)acrylate or a polymer thereof can be modified with one or more compounds of formula $X'-Y'-Z'$ by any suitable means at any suitable temperature. For example, the grafted glycidyl (meth)acrylate or a polymer thereof can be modified by mixing, contacting, submersing, or the like, the grafted glycidyl (meth)acrylate or a polymer thereof with a solution comprising the one or more compounds of formula $X'-Y'-Z'$ or multiple solutions comprising a compound of formula $X'-Y'-Z'$. The solution comprising the one or more compounds of formula $X'-Y'-Z'$ can comprise a solvent such as, for example, water, alcohols (e.g., ethanol or methanol), sulfoxides, sulfides, acetates, ethers, amides, nitriles, or a combination thereof. In some embodiments, the solution comprising the

one or more compounds of formula $X'-Y'-Z'$ comprises dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), and/or dimethyl sulfoxide (DMSO), optionally in combination with water. The grafted glycidyl (meth)acrylate or a polymer thereof can be modified at a temperature of 25 °C to 200 °C, 25 °C to 150 °C, 25 °C to 100 °C, 50 °C to 200 °C, 50 °C to 150 °C, 50 °C to 100 °C. Typically, the glycidyl (meth)acrylate or a polymer thereof is grafted on the polymeric support at a temperature of about 75 °C to 100 °C.

[0053] The solution comprising the one or more compounds of formula $X'-Y'-Z'$ can comprise any suitable amount of the one or more compounds of formula $X'-Y'-Z'$. For example, the solution comprising the one or more compounds of formula $X'-Y'-Z'$ can comprise from about 0.1 wt.% to about 50 wt.%, about 0.1 wt.% to about 40 wt.%, about 0.1 wt.% to about 30 wt.%, about 0.1 wt.% to about 20 wt.%, about 1 wt.% to about 50 wt.%, about 1 wt.% to about 40 wt.%, about 1 wt.% to about 30 wt.%, about 1 wt.% to about 20 wt.%, about 5 wt.% to about 50 wt.%, about 5 wt.% to about 40 wt.%, about 5 wt.% to about 30 wt.%, or about 5 wt.% to about 20 wt.% of the one or more compounds of formula $X'-Y'-Z'$.

[0054] The modification of the grafted glycidyl (meth)acrylate or a polymer thereof can be facilitated by an acid (e.g., a Bronsted acid or a Lewis acid) or a base (e.g., a Bronsted base or a Lewis base). In some embodiments, the modification of the grafted glycidyl (meth)acrylate or a polymer thereof is facilitated by an amine base (e.g., trimethylamine, trimethylamine, diisopropylethylamine, or the like).

[0055] The modified grafted glycidyl (meth)acrylate or a polymer thereof (i.e., the material described herein) can be washed with water, an organic solvent (e.g., an alcohol such as ethanol or methanol, a sulfoxide, a sulfide, an acetate, an ether, an amide, a nitrile, or a combination thereof), an acidic solution (e.g., aqueous hydrochloric acid or aqueous sulfuric acid), a basic solution (e.g., aqueous tetramethylammonium hydroxide or aqueous ammonium hydroxide), or a combination thereof. In some embodiments, the modified grafted glycidyl (meth)acrylate or a polymer thereof (i.e., the material described herein) is washed with an acidic solution (e.g., aqueous hydrochloric acid or aqueous sulfuric acid) followed by a basic solution (e.g., aqueous tetramethylammonium hydroxide or aqueous ammonium hydroxide).

[0056] The modified grafted glycidyl (meth)acrylate or a polymer thereof (i.e., the material described herein), or an intermediate thereof, can be dried by any suitable means. For example, the modified grafted glycidyl (meth)acrylate or a polymer thereof (i.e., the

material described herein), or an intermediate thereof, can be dried by air, elevated temperatures, a desiccant, sieves, or a combination thereof.

[0057] The materials described herein can be used in any suitable industrial application for any suitable purpose. For example, the materials described herein can be used in water purification applications, wastewater treatment applications, organic solvent treatment applications, mining applications, electronic (e.g., microelectronic) applications, papermaking applications, pharmaceutical applications, biomedical applications, energy applications (e.g., as separators in fuel cells or batteries), or metallurgy applications. Generally, the materials described herein are used to selectively remove one or more metal ions from a fluid (i.e., solution). The fluid can be any suitable liquid containing a solvent (e.g., water, alcohols, sulfoxides, sulfides, acetates, ethers, ketones, amides, nitriles, or a combination thereof) and one or more metal ions. In certain embodiments, the fluid (i.e., solution) is an aqueous solution. In some embodiments, the fluid (i.e., solution) comprises an organic solvent such as, for example, alcohols (e.g., ethanol or methanol), sulfoxides, sulfides, acetates, ethers, ketones, amides, nitriles, or a combination thereof. In certain embodiments, the fluid comprises cyclohexanone (CHN), propylene glycol methyl ether (PGME), propylene glycol methyl ether acetate (PGMEA), ethyl lactate, or a combination thereof.

[0058] In some embodiments, the materials described herein can be used in a method of removing one or more metal ions from a solution comprising (i) passing the solution through the material or (ii) contacting the solution with the material. For example, the material can be used as a filter, porous media, chromatographic resin, membrane, or the like through which the solution passes or is contacted with to remove one or more metal ions. Thus, the invention further provides a method of removing one or more metal ions from a solution comprising (i) passing the solution through or (ii) contacting the solution with a material comprising a glycidyl (meth)acrylate of Formula (I), Formula (Ia), Formula (II), or Formula (IIa). In some embodiments, the invention provides a method of removing one or more metal ions from a solution comprising (i) passing the solution through or (ii) contacting the solution with one or more materials comprising a glycidyl (meth)acrylate of Formula (I), Formula (Ia), Formula (II), or Formula (IIa).

[0059] The method can be used to remove any suitable ion. Alternatively, or additionally, the method can be used to allow any suitable ion to pass through the material. For example, the method can be used to selectively remove one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium,

manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof. Alternatively, or additionally, the method can be used to selectively allow one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof. In certain embodiments, the method selectively allows for lithium to pass through the material and removes one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof.

[0060] The method can remove any suitable amount of the one or more metal ions from the solution. For example, the method can remove at least 40% of the one or more metal ions from the solution, at least 50% of the one or more metal ions from the solution, at least 60% of the one or more metal ions from the solution, at least 70% of the one or more metal ions from the solution, at least 80% of the one or more metal ions from the solution, or at least 90% of the one or more metal ions from the solution. In some embodiments, the method removes at least 50% of one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof. In certain embodiments, the method removes at least 60% of one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof. In preferred embodiments, the method removes at least 70% of one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof.

[0061] In some embodiments, the solution that passes through or is contacted with the material is the desirable product of the methods described herein. Thus, in such embodiments, the method can further comprise recovering the solution (e.g., aqueous solution or organic solution) that has been passed through or contacted with the material.

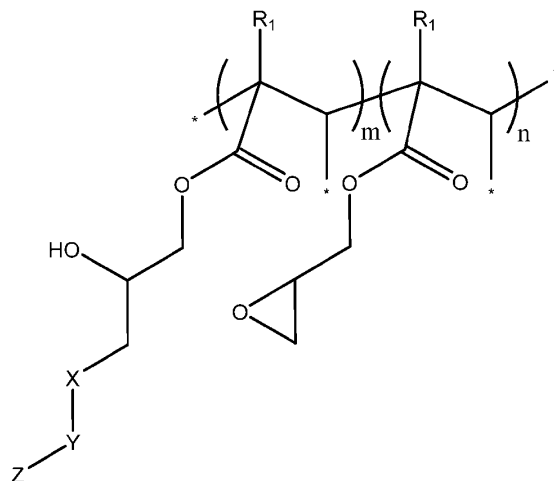
Without wishing to be bound by any particular theory, it is believed that when smaller metal ions such as lithium and/or sodium are desired, the recovered solution will be the desired product since smaller metal ions such as lithium and/or sodium are more likely to pass through the materials described herein.

[0062] In other embodiments, the one or more metal ions removed from the solution are the desirable product of the method described herein. Thus, in these embodiments, the method can further comprise recovering the one or more metal ions removed from the solution. The one or more metal ions can be recovered by any suitable means. For example the material containing the one or more metal ions can be washed with a recovery solution. Without wishing to be bound by any particular theory, it is believed that when larger metal ions such as magnesium, aluminum, potassium, calcium, manganese, iron, barium, etc. are desired, and these desired metal ions will remain in the material because larger metal ions are less likely to pass through the materials described herein.

[0063] Aspects, including embodiments, of the invention described herein may be beneficial alone or in combination, with one or more other aspects or embodiments. Without limiting the foregoing description, certain non-limiting embodiments of the disclosure numbered 1-24 are provided below. As will be apparent to those of skill in the art upon reading this disclosure, each of the individually numbered embodiments may be used or combined with any of the preceding or following individually numbered embodiments. This is intended to provide support for all such combinations of embodiments and is not limited to combinations of embodiments explicitly provided below:

EMBODIMENTS

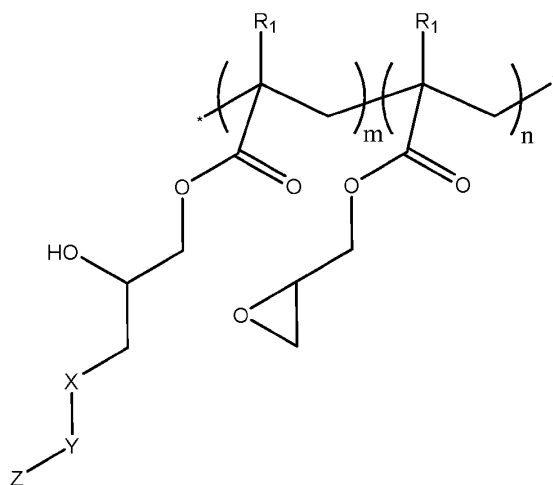
[0064] (1) In embodiment (1) is presented a material comprising a glycidyl (meth)acrylate of Formula (I):



Formula (I),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R_1 independently is hydrogen or methyl, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl, R_3 is hydrogen or C_{1-6} alkyl, each Z independently is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted, and each $*$ independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one $*$ is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp^3-sp^3 carbon-carbon bond.

[0065] (2) In embodiment (2) is presented the material of embodiment (1), wherein the material comprises a glycidyl (meth)acrylate of Formula (Ia):



Formula (Ia),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R_1 independently is hydrogen or methyl, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl, R_3 is hydrogen or C_{1-6} alkyl, each Z independently is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted, and each $*$ independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one $*$ is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp^3-sp^3 carbon-carbon bond.

[0066] (3) In embodiment (3) is presented the material of embodiment (1) or embodiment (2), wherein each R_1 is methyl.

[0067] (4) In embodiment (4) is presented the material of any one of embodiments (1)-(3), wherein m is an integer from 1 to 1000.

[0068] (5) In embodiment (5) is presented the material of any one of embodiments (1)-(4), wherein n is an integer from 1 to 1000.

[0069] (6) In embodiment (6) is presented the material of any one of embodiments (1)-(5), wherein each X independently is $-NR_2-$ and R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl.

[0070] (7) In embodiment (7) is presented the material of any one of embodiments (1)-(5), wherein each X is $-S-$.

[0071] (8) In embodiment (8) is presented the material of any one of embodiments (1)-(7), wherein each Z independently is phenyl, furyl, benzofuranyl, thiophenyl, benzothiophenyl, pyrrolyl, indolyl, isoindolyl, azaindolyl, pyridyl, quinolyl, isoquinolyl, oxazolyl, isooxazolyl, benzoxazolyl, pyrazolyl, imidazolyl, benzimidazolyl, thiazolyl, benzothiazolyl, isothiazolyl, pyridazyl, pyrimidinyl, pyrazinyl, triazinyl, cinnolyl, phthalazinyl, quinazolinyl, morpholyl, pyrrolidinyl, pyrrolidinyl, piperidinyl, hydantoinyl, valerolactamyl, oxiranyl, oxetanyl, tetrahydrofuranyl, tetrahydropyranyl, tetrahydropyridinyl, tetrahydroprimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, tetrahydropyrimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, piperazinyl, or dihydropyrimidinyl, each of which is optionally substituted.

[0072] (9) In embodiment (9) is presented the material of any one of embodiments (1)-(8), wherein at least one Z is halogenated aryl or halogenated heteroaryl.

[0073] (10) In embodiment (10) is presented the material of any one of embodiments (1)-(9), wherein at least one Z is fluorinated aryl or fluorinated heteroaryl.

[0074] (11) In embodiment (11) is presented the material of any one of embodiments (1)-(10), wherein at least one Z is optionally substituted pyridyl.

[0075] (12) In embodiment (12) is presented the material of any one of embodiments (1)-(11), wherein the bond to a remainder of the material is a bond to a macromolecular support selected from a membrane, a fibrous media, a polymeric coating or material, a metal organic framework, a monolith support, a bead, a filter, or a resin, and wherein the macromolecular support is bound via a sp³-sp³ carbon-carbon bond.

[0076] (13) In embodiment (13) is presented the material of embodiment (12), wherein the macromolecular support comprises gelatin, alginate, starch, polyethylene, polypropylene, nylon, polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, polyethylene/polypropylene oxide, polyacrylonitrile, poly(meth)acrylate, poly(meth)acrylamide, polyamide, polyimide, polyester, cellulose, polystyrene, or a combination thereof.

[0077] (14) In embodiment (14) is presented the material of embodiment (12), wherein the macromolecular support comprises polyvinylidene fluoride, polyethylene, polypropylene, nylon, or a combination thereof.

[0078] (15) In embodiment (15) is presented a method of making a material of any one of embodiments (1)-(14), the method comprising:

(i) (a) irradiating (e.g., radiating) a polymeric support with an irradiation (e.g., a radiation) source and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof or (b) generating radicals on a polymeric support in the presence of glycidyl (meth)acrylate or a polymer thereof, wherein the polymeric support comprises one or more C–H aliphatic bonds, to graft the glycidyl (meth)acrylate or a polymer thereof on the polymeric support via one or more sp³-sp³ carbon-carbon bonds, and

(ii) modifying the grafted glycidyl (meth)acrylate or a polymer thereof with one or more compounds of formula X'–Y'–Z', wherein X' is HO–, HOOC–, HS–, piperazinyl, or HNR₂–, R₂ is hydrogen, aryl, heteroaryl, C₁₋₆ alkyl aryl, C₁₋₆ alkyl heteroaryl, or C₁₋₆ alkyl, Y' is optionally present and is –NR₃– or optionally substituted C₁₋₆ alkyl, R₃ is hydrogen or C₁₋₆ alkyl, and Z' is aryl, heteroaryl, or C₂₋₆ heterocyclyl, each of which is optionally substituted.

[0079] (16) In embodiment (16) is presented the method of embodiment (15), wherein the method comprises irradiating (e.g., radiating) the polymeric support with E-beam irradiation, gamma irradiation, X-ray irradiation, or a combination thereof and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof.

[0080] (17) In embodiment (17) is presented the method of embodiment (15), wherein the method comprises generating radicals on the polymeric support with UV light, plasma, corona discharge, a chemical initiator, or a combination thereof in the presence of glycidyl (meth)acrylate or a polymer thereof.

[0081] (18) In embodiment (18) is presented the method of any one of embodiments (15)-(17), wherein steps (i) and/or (ii) are performed in an environment with an O₂ concentration of 50 ppm or less.

[0082] (19) In embodiment (19) is presented a method of removing one or more metal ions from a solution comprising (i) passing the solution through the material of any one of embodiments (1)-(14) or (ii) contacting the solution with the material of any one of embodiments (1)-(14).

[0083] (20) In embodiment (20) is presented the method of embodiment (19), wherein the solution is an aqueous solution.

[0084] (21) In embodiment (21) is presented the method of embodiment (19) or embodiment (20), wherein the solution comprises an organic solvent.

[0085] (22) In embodiment (22) is presented the method of any one embodiment (19)-(21), wherein the method removes at least 50% of one or more metal ions selected from

sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof.

[0086] (23) In embodiment (23) is presented the method of any one embodiments (19)-(21), wherein the method removes at least 60% of one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof.

[0087] (24) In embodiment (24) is presented the method of any one embodiments (19)-(21), wherein the method removes at least 70% of one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof.

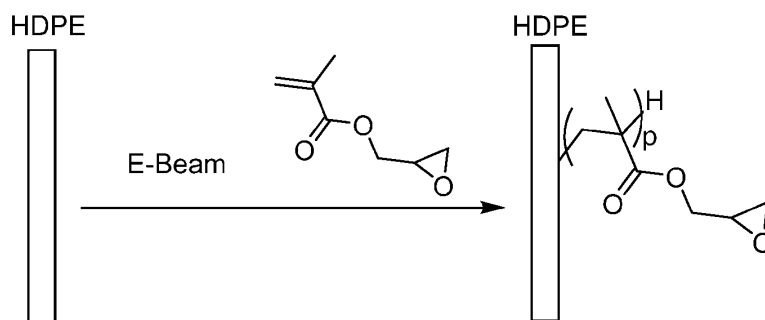
EXAMPLES

[0088] These following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

[0089] This example provides an exemplary experimental procedure for the preparation of a glycidyl methacrylate grafted roll, which is summarized in Scheme 1.

Scheme 1.



[0090] High density polyethylene (HDPE) (1-micron) substrate was fed into an E-Beam where it was irradiated, co-wound with the interleaf, and dipped into a coating solution containing glycidyl methacrylate, and rewound to form a glycidyl methacrylate grafted roll. The coating solution was prepared by dissolving glycidyl methacrylate (2 kg) in methanol (18

kg) and mixed for 10 minutes to form a 10 wt.% solution of glycidyl methacrylate in methanol. The E-beam and grafting conditions are set forth in Table 1 below.

Table 1. E-Beam and Grafting Conditions

Process	Specifications
Line Speed (ft/min)	34
Dosage (mRads)	12
Unwind Tension (lbs)	3.5
Rewind Tension (lbs)	8.0
Pressure Roller Setting (psi)	5.5 on both sides
O ₂ at Peel (ppm)	<50
O ₂ at Rewind (ppm)	<50
O ₂ at Window (ppm)	<50

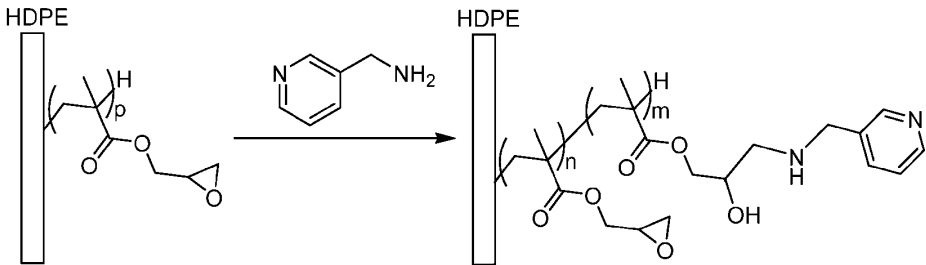
[0091] As noted in Table 1, all unwind, irradiation, monomer impregnation, and rewind processes were executed in an environment with an O₂ level of <50 ppm. Weight change, critical water surface tension (CWST), and FTIR were used to confirm grafting of glycidyl methacrylate on the HDPE substrate.

[0092] The glycidyl methacrylate grafted roll was washed with methanol using a recycled trickle wash for 4 hours followed by a deionized water trickle wash for 6 hours to remove any residual non-grafted monomer, oligomer, and polymer. After drying the glycidyl methacrylate grafted roll, the glycidyl methacrylate uptake was determined to be approximately 100-140 percent by weight based on the HDPE substrate.

EXAMPLE 2

[0093] This example provides an exemplary experimental procedure for the preparation of a material of Formula (I), described herein, which is summarized in Scheme 2.

Scheme 2.



[0094] 3-picolylamine (10 g) was dissolved in 90 g water/DMSO (1:1) and the resulting solution was added to a 12" by 12" strip of the glycidyl methacrylate grafted HDPE and the combination was heated to 85 °C for 24 hours. After cooling the glycidyl methacrylate grafted HDPE and removing the remaining solution, the resulting media was washed with isopropanol and water several times. The washed media was then dried in an oven at 65 °C for 2 hours. The uptake of 3-picolylamine was determined to be approximately 10-30 percent by weight.

[0095] The washed surface modified media was subsequently cleaned by soaking the media in methanol for 30 minutes, 50% isopropanol or methanol for 30 minutes, and deionized water for 2 hours. After soaking the surface modified media in the various solvents, the surface modified media was soaked in 1% hydrochloric acid for 2 hours and then rinsed with deionized water to obtain a pH of 7. The protonated functional groups on the media were subsequently deprotonated by soaking the media in tetramethylammonium hydroxide (1%) for 2 hours and then rinsed with deionized water to obtain a pH of 7. The resulting material was then trickle washed with deionized water for 1 hour and dried in an oven at 65 °C for 2 hours. The uptake of 3-picolylamine after cleaning was determined to be approximately 10-30 percent by weight.

[0096] The 3-picolylamine modified glycidyl methacrylate grafted HDPE was analyzed by scanning electron microscope (SEM) and the top surface image and cross-sectional image are set forth in FIGs. 1A and 1B, respectively.

EXAMPLE 3

[0097] This example demonstrates the metal removal efficiency of the material of Example 2, described herein.

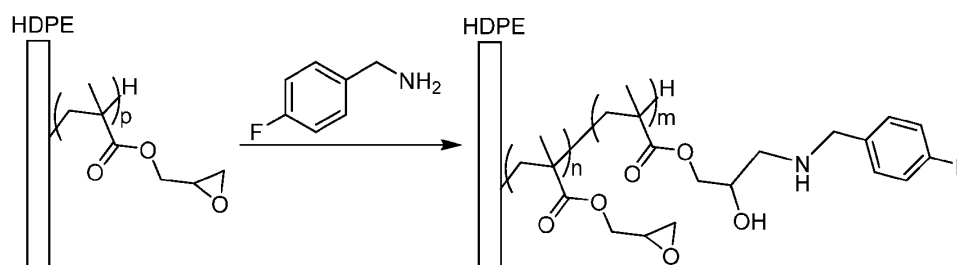
[0098] Metal removal efficiency (MRE) testing was performed using a punched 47 mm disc of the HDPE coated material of Example 2. A 20-30 mL solution of (a) cyclohexanone (CHN), (b) propylene glycol methyl ether (PGME), or (c) propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) containing 1 ppb of each metal impurity (i.e., titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver) was passed through the disc and the resulting metal ion concentrations were measured by inductively coupled plasma - mass spectrometry (ICP-MS). The metal removal efficiency (i.e., the percent concentration removed) for three separate trials for each of the solvents (a)-(c) were calculated and the results are plotted in FIGs. 2-4, respectively.

[0099] As is apparent from the results set forth in FIGs. 2-4, the HDPE coated material of Example 2 removed greater than 80% of titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver, and in certain instances vanadium, from a variety of solvents. In addition, the HDPE coated material of Example 2 was particularly effective at removing chromium, manganese, iron, cobalt, nickel, copper, and zinc from all solvents tested, exhibiting greater than 90% MRE in all instances.

EXAMPLE 4

[00100] This example provides an exemplary experimental procedure for the preparation of a material of Formula (I), described herein, which is summarized in Scheme 3.

Scheme 3.



[0100] 4-fluorobenzylamine (10 g) was dissolved in 90 g DMSO and the resulting solution was added to a 12" by 12" strip of the glycidyl methacrylate grafted HDPE and the combination was heated to 85 °C for 24 hours. After cooling the glycidyl methacrylate grafted HDPE and removing the remaining solution, the resulting media was washed with isopropanol and water several times. The washed media was then dried in an oven at 65 °C for 2 hours. The uptake of 4-fluorobenzylamine was determined to be approximately 10-30 percent by weight.

[0101] The washed surface modified media was subsequently cleaned by soaking the media in methanol for 30 minutes, 50% isopropanol or methanol for 30 minutes, and deionized water for 2 hours. After soaking the surface modified media in the various solvents, the surface modified media was soaked in 1% hydrochloric acid for 2 hours and then rinsed with deionized water to obtain a pH of 7. The protonated functional groups on the media were subsequently deprotonated by soaking the media in tetramethylammonium hydroxide (1%) for 2 hours and then rinsed with deionized water to obtain a pH of 7. The resulting material was then trickle washed with deionized water for 1 hour and dried in an

oven at 65 °C for 2 hours. The uptake of 4-fluorobenzylamine after cleaning was determined to be approximately 10-30 percent by weight.

[0102] The 4-fluorobenzylamine modified glycidyl methacrylate grafted HDPE was confirmed by scanning electron microscope (SEM).

EXAMPLE 5

[0103] This example demonstrates the metal removal efficiency of the material of Example 4, described herein.

[0104] Metal removal efficiency (MRE) testing was performed using a punched 47 mm disc of the HDPE coated material of Example 4. A 20-30 mL solution of (a) cyclohexanone (CHN), (b) propylene glycol methyl ether (PGME), or (c) propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) containing 1 ppb of each metal impurity (i.e., titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver) was passed through the disc and the resulting metal ion concentrations were measured by inductively coupled plasma - mass spectrometry (ICP-MS). The metal removal efficiency (i.e., the percent concentration removed) for three separate trials for each of the solvents (a)-(c) were calculated and the results are plotted in FIGs. 5-7, respectively.

[0105] As is apparent from the results set forth in FIGs. 5-7, the HDPE coated material of Example 4 removed greater than 80% of titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver, and in certain instances vanadium, from a variety of solvents. In addition, the HDPE coated material of Example 4 was particularly effective at removing titanium, chromium, manganese, iron, cobalt, nickel, copper, and zinc from all solvents tested, exhibiting greater than 90% MRE in all instances.

EXAMPLE 6

[0106] This example demonstrates the metal removal efficiency of a composite material comprising the material of Example 2 and the material of Example 4, described herein.

[0107] Metal removal efficiency (MRE) testing was performed using a punched 47 mm disc of a double layer including one layer of the HDPE coated material of Example 2 and one layer of the HDPE coated material of Example 4. A 20-30 mL solution of (a) cyclohexanone (CHN), (b) propylene glycol methyl ether (PGME), or (c) propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) containing 1 ppb of each metal impurity (i.e., titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver) was passed through the disc and the resulting metal ion concentrations were measured by inductively

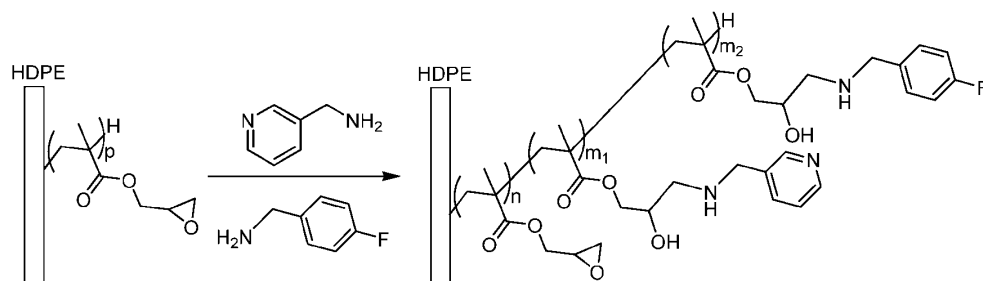
coupled plasma - mass spectrometry (ICP-MS). The metal removal efficiency (i.e., the percent concentration removed) for three separate trials for each of the solvents (a)-(c) were calculated and the results are plotted in FIGs. 8-10, respectively. FIGs 8-10 designated with an "A", i.e., FIG. 8A, 9A, and 10A, had an orientation of one layer of the HDPE coated material of Example 2 on top and one layer of the HDPE coated material of Example 4 on bottom, i.e., the solution passed through the one layer of the HDPE coated material of Example 2 first. FIGs 8-10 designated with an "B", i.e., FIG. 8B, 9B, and 10B, had an orientation of one layer of the HDPE coated material of Example 4 on top and one layer of the HDPE coated material of Example 2 on bottom, i.e., the solution passed through the one layer of the HDPE coated material of Example 4 first.

[0108] As is apparent from the results set forth in FIGs. 8-10, the composite material comprising the material of Example 2 and the material of Example 4 provides a MRE that is consistent with the performance of the material of Example 2 and the material of Example 4.

EXAMPLE 7

[0109] This example provides an exemplary experimental procedure for the preparation of a material of Formula (I), described herein, which is summarized in Scheme 4.

Scheme 4.



[0110] 3-picolylamine (5 g) and 4-fluorobenzylamine (5 g) were dissolved in 90 g water/DMSO (1:1) and the resulting solution was added to a 12" by 12" strip of the glycidyl methacrylate grafted HDPE and the combination was heated to 85 °C for 24 hours. After cooling the glycidyl methacrylate grafted HDPE and removing the remaining solution, the resulting media was washed with isopropanol and water several times. The washed media was then dried in an oven at 65 °C for 2 hours. The uptake of 3-picolylamine and 4-fluorobenzylamine was determined to be approximately 10-30 percent by weight.

[0111] The washed surface modified media was subsequently cleaned by soaking the media in methanol for 30 minutes, 50% isopropanol or methanol for 30 minutes, and

deionized water for 2 hours. After soaking the surface modified media in the various solvents, the surface modified media was soaked in 1% hydrochloric acid for 2 hours and then rinsed with deionized water to obtain a pH of 7. The protonated functional groups on the media were subsequently deprotonated by soaking the media in tetramethylammonium hydroxide (1%) for 2 hours and then rinsed with deionized water to obtain a pH of 7. The resulting material was then trickle washed with deionized water for 1 hour and dried in an oven at 65 °C for 2 hours. The uptake of 3-picolyamine and 4-fluorobenzylamine after cleaning was determined to be approximately 10-30 percent by weight.

[0112] The 3-picolyamine- and 4-fluorobenzylamine-modified glycidyl methacrylate grafted HDPE was confirmed by scanning electron microscope (SEM).

EXAMPLE 8

[0113] This example demonstrates the metal removal efficiency of the material of Example 7, described herein.

[0114] Metal removal efficiency (MRE) testing was performed using a punched 47 mm disc of the HDPE coated material of Example 7. A 20-30 mL solution of (a) cyclohexanone (CHN), (b) propylene glycol methyl ether (PGME), or (c) propylene glycol methyl ether acetate (PGMEA) / ethyl lactate (EL) containing 1 ppb of each metal impurity (i.e., titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver) was passed through the disc and the resulting metal ion concentrations were measured by inductively coupled plasma - mass spectrometry (ICP-MS). The metal removal efficiency (i.e., the percent concentration removed) for three separate trials for each of the solvents (a)-(c) were calculated and the results are plotted in FIGs. 11-13, respectively.

[0115] As is apparent from the results set forth in FIGs. 11-13, the HDPE coated material of Example 7 removed greater than 80% of titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver, and in certain instances vanadium, from a variety of solvents. In addition, the HDPE coated material of Example 7 was particularly effective at removing titanium, manganese, iron, cobalt, nickel, copper, zinc, and silver from all solvents tested, exhibiting greater than 90% MRE in all instances.

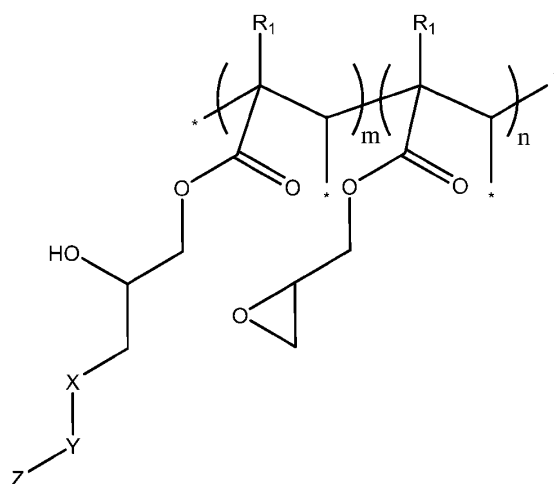
[0116] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0117] The use of the terms “a” and “an” and “the” and “at least one” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term “at least one” followed by a list of one or more items (for example, “at least one of A and B”) is to be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0118] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

CLAIMS:

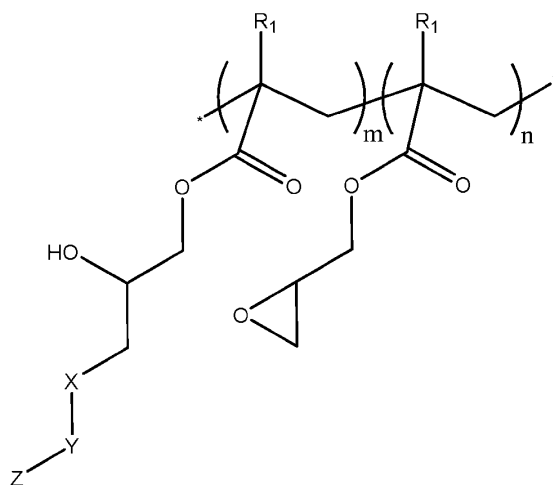
1. A material comprising a glycidyl (meth)acrylate of Formula (I):



Formula (I),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R_1 independently is hydrogen or methyl, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl, R_3 is hydrogen or C_{1-6} alkyl, each Z independently is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted, and each $*$ independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one $*$ is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp^3 - sp^3 carbon-carbon bond.

2. The material of claim 1, wherein the material comprises a glycidyl (meth)acrylate of Formula (Ia):



Formula (Ia),

or a salt thereof, wherein m is an integer from 1 to 10000, n is an integer from 0 to 10000, each R_1 independently is hydrogen or methyl, each X independently is $-O-$, $-COO-$, $-S-$, piperazinyl, or $-NR_2-$, R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl, each Y independently is optionally present and is $-NR_3-$ or optionally substituted C_{1-6} alkyl, R_3 is hydrogen or C_{1-6} alkyl, each Z independently is aryl, heteroaryl, or C_{2-6} heterocyclyl, each of which is optionally substituted, and each $*$ independently represents hydrogen, a terminating group, or a bond to a remainder of the material, provided that at least one $*$ is a bond to the remainder of the material, and wherein the remainder of the material is bound via a sp^3-sp^3 carbon-carbon bond.

3. The material of claim 1 or claim 2, wherein each R_1 is methyl.
4. The material of any one of claims 1-3, wherein m is an integer from 1 to 1000.
5. The material of any one of claims 1-4, wherein n is an integer from 1 to 1000.
6. The material of any one of claims 1-5, wherein each X independently is $-NR_2-$ and R_2 is hydrogen, aryl, heteroaryl, C_{1-6} alkyl aryl, C_{1-6} alkyl heteroaryl, or C_{1-6} alkyl.
7. The material of any one of claims 1-5, wherein each X is $-S-$.

8. The material of any one of claims 1-7, wherein each Z independently is phenyl, furyl, benzofuranyl, thiophenyl, benzothiophenyl, pyrrolyl, indolyl, isoindolyl, azaindolyl, pyridyl, quinoliny, isoquinoliny, oxazolyl, isooxazolyl, benzoxazolyl, pyrazolyl, imidazolyl, benzimidazolyl, thiazolyl, benzothiazolyl, isothiazolyl, pyridaziny, pyrimidinyl, pyraziny, triaziny, cinnoliny, phthalaziny, quinazoliny, morpholiny, pyrrolidinonyl, pyrrolidinyl, piperidinyl, hydantoinyl, valerolactamyl, oxiranyl, oxetanyl, tetrahydrofuranly, tetrahydropyranyl, tetrahydropyridinyl, tetrahydropyrimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, tetrahydropyrimidinyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, piperaziny, or dihydropyrimidinyl, each of which is optionally substituted.

9. The material of any one of claims 1-8, wherein at least one Z is halogenated aryl or halogenated heteroaryl.

10. The material of any one of claims 1-9, wherein at least one Z is fluorinated aryl or fluorinated heteroaryl.

11. The material of any one of claims 1-10, wherein at least one Z is optionally substituted pyridyl.

12. The material of any one of claims 1-11, wherein the bond to a remainder of the material is a bond to a macromolecular support selected from a membrane, a fibrous media, a polymeric coating or material, a metal organic framework, a monolith support, a bead, a filter, or a resin, and wherein the macromolecular support is bound via a sp³-sp³ carbon-carbon bond.

13. The material of claim 12, wherein the macromolecular support comprises gelatin, alginate, starch, polyethylene, polypropylene, nylon, polyvinylidene fluoride, polyethylene oxide, polypropylene oxide, polyethylene/polypropylene oxide, polyacrylonitrile, poly(meth)acrylate, poly(meth)acrylamide, polyamide, polyimide, polyester, cellulose, polystyrene, or a combination thereof.

14. A method of making a material of any one of claims 1-13, the method comprising:

(i) (a) irradiating a polymeric support with an irradiation source and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof or (b)

generating radicals on a polymeric support in the presence of glycidyl (meth)acrylate or a polymer thereof, wherein the polymeric support comprises one or more C–H aliphatic bonds, to graft the glycidyl (meth)acrylate or a polymer thereof on the polymeric support via one or more sp³-sp³ carbon-carbon bonds, and

(ii) modifying the grafted glycidyl (meth)acrylate or a polymer thereof with one or more compounds of formula X'–Y'–Z', wherein X' is HO–, HOOC–, HS–, piperazinyl, or HNR₂–, R₂ is hydrogen, aryl, heteroaryl, C₁₋₆ alkyl aryl, C₁₋₆ alkyl heteroaryl, or C₁₋₆ alkyl, Y' is optionally present and is –NR₃– or optionally substituted C₁₋₆ alkyl, R₃ is hydrogen or C₁₋₆ alkyl, and Z' is aryl, heteroaryl, or C₂₋₆ heterocyclyl, each of which is optionally substituted.

15. The method of claim 14, wherein the method comprises irradiating the polymeric support with E-beam irradiation, gamma irradiation, X-ray irradiation, or a combination thereof and subsequently impregnating the polymeric support with glycidyl (meth)acrylate or a polymer thereof.

16. The method of claim 14, wherein the method comprises generating radicals on the polymeric support with UV light, plasma, corona discharge, a chemical initiator, or a combination thereof in the presence of glycidyl (meth)acrylate or a polymer thereof.

17. A method of removing one or more metal ions from a solution comprising (i) passing the solution through the material of claim 1 or (ii) contacting the solution with the material of any one of claims 1-13.

18. The method of claim 17, wherein the solution is an aqueous solution.

19. The method of claim 17 or claim 18, wherein the solution comprises an organic solvent.

20. The method of any one of claims 17-19, wherein the method removes at least 50% of one or more metal ions selected from sodium, magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, molybdenum, silver, cadmium, tin, barium, tungsten, strontium, lead, or a combination thereof.