CROSSLINKED SPIROBISINDANE POLYMERS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/565,288, filed March 14, 2024, which is incorporated in its entirety herein for all purposes.

BACKGROUND OF THE INVENTION

[0002] Over the past decades, lithium-ion batteries (Li-ion batteries) have developed as the dominant high-energy chemistry due to their uniquely high energy density while maintaining high power and cyclability at acceptable prices. The energy density of current commercial Li-ion battery chemistries is however approaching the technology's theoretical limit, whereas demand for higher energy density batteries at lower unit cost is increasing with the rapid trend towards electrification of the transport and energy industries. There is indeed a need for batteries with improved capacity, long cycle life and high stability. Replacing graphite anodes in Li-ion with lithium metal anodes provides an opportunity to significantly increase the energy density of lithium batteries. However, after repetitive charge-discharge cycles, lithium metal batteries suffer from irreversible capacity loss driven by electrolyte depletion and loss of lithium inventory due to parasitic reactivity between the highly reactive lithium metal anode and the electrolyte components. This process contributes to local non-uniformities in the lithium anode surface, propagating further uneven plating and stripping and resulting in physically isolated "dead" lithium. Further, uneven lithium plating increases the risk of dendrite formation, which can cause thermal runaway resulting in catastrophic cell failure, posing a significant hurdle to the commercialization of lithium metal batteries. Mitigation of dendrite formation in lithium metal batteries is critical to enabling their safe, stable use in commercial applications.

[0003] Battery separators are a critical component of Li-ion batteries since they isolate the electrodes, providing ion transport through large pores filled with electrolyte and insulating electronic conductivity that would otherwise induce a short circuit. Whereas separators are not involved directly in cell reactions, their physical properties play an important role in determining the performance of the battery including energy density, power density, and safety. Importantly, separators' mechanical integrity throughout the entire lifetime of the battery cell is critical for prevention of internal short circuit.

[0004] Several porous membrane separator materials and composites are currently utilized in Li-ion batteries, such as separators made of made of polyolefin, for example polyethylene (PE), polypropylene (PP) and polypropylene-polyethylene-polypropylene (PP/PE/PP), as well as ceramic-coated separators, which include PP, PE or multilayer porous substrates with at least one surface coated with a ceramic composite layer. As described in US 6,432,583 (Celgard Inc.), the ceramic composite layer is intended to block dendrite growth and to prevent electronic shorting. Although ceramic coated separators have been successfully utilized in Li-ion batteries to improve mechanical properties, their utility is limited in lithium metal batteries due to parasitic reactions induced at the anode by the binding materials which host the ceramic coatings.

[0005] WO 2018/106957 (Sepion Technologies, Inc et al.) describes the application of porous polymers (10-40% porosity, 0.5-2.0 nm pores) as templates that deliver solution-processed precursors of solid-state plus halide containing salts as a conformal coating between the Li-metal surface and the separator surface, in order to increase separator wettability and to increase Li-ion concentration and mobility at the separator-anode interface. The document also describes electrochemical cells including separators comprising several layers: a first polymer layer, comprising a planar species and a linker. The separator may also comprise a porous support made of PP or PE, laminated to the first polymer layer. The separator may also comprise a second membrane layer laminated to the porous support, such second layer comprising a ceramic material.

[0006] The use of Polymers of Intrinsic Microporosity (PIMs) as a selective battery membrane has been investigated. PIMs are composed of fused rings providing rigidity and sites of contortion, which may be provided by spiro-centers, by bent or bridged ring moieties, or by similar structural components which serve as a barrier preventing conformational relaxation of polymer chains. PIMs have been described and studied since 2006, as they create continuous networks of interconnected voids used as gas separation membranes, hydrogen storage materials, adsorbents and heterogeneous catalysts. The intrinsic microporosity of PIMs is defined as a continuous network of interconnected intermolecular voids, which form as a direct consequence of the shape and rigidity of the component macromolecules. Notably, the article of Li et al. (Nano Lett. 2015, 15, 5724-5729) describes the use of PIMs as a membrane platform for achieving high-flux, ion-selective transport in nonaqueous electrolytes.

[0007] As lithium metal is highly reactive, a solid-electrolyte-interphase (SEI) forms at the interface of the electrode and the adjacent electrolyte-filled separator. The composition and morphology of the SEI impacts the performance of the electrochemical cell. On one hand, the consumption of part of the lithium inventory inherent to the *in situ* SEI formation process reduces the coulombic efficiency of the electrochemical cell. On the other hand, optimal SEI limits the further decomposition of electrolyte components and improves lithium-ion transport at the electrode-separator interface, improving the cycling performance and service life of the batteries.

[0008] Artificial SEI layers have been investigated in order to limit lithium inventory and electrolyte component depletion processes at the surface of anode materials. One of the approaches is based on the use of a layer of PIMs which is coated on porous supports. Notably, WO 2020/037246 A1 (The Regents of the University of California) describes microporous ladder polymer according to the formula -[A-AB-B]- containing amine-functionalized monomer segments, amidoxime functionalized monomer segments, or a combination thereof, such microporous polymers being used in the separator which may comprise one or more support material such as glass fibers. Thin films of microporous polymers on porous supports, such as a polyolefin battery separator (e.g., Celgard) are described in the examples. The article of Chengyin Fu et al. (Nature Materials, April 2020) describes a lithium electrode laminated with a TBAF@PIM-1 coated polyolefin separator, i.e., a separator coated with microporous polymer host (e.g., PIM-1) in combination with tetrabutylammonium fluoride (TBAF), with the separator (Celgard 2325). The coated separator was then assembled in either Li–Li or Li–NMC-622 cells along with a carbonate electrolyte containing an ionizable lithium salt (e.g., $LiPF_6$). The composites are described to act as dendrite-suppressing solid-ion conductors (SICs) in lithium metal batteries. What is needed are new polymers for separator coatings. Surprisingly, the present invention meets this and other needs.

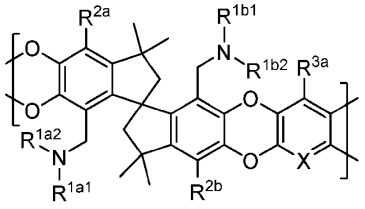
BRIEF SUMMARY OF THE INVENTION

[0009] In one embodiment, the present invention provides a cross-linkable polymer composition comprising:

a polymer of Formula (I):

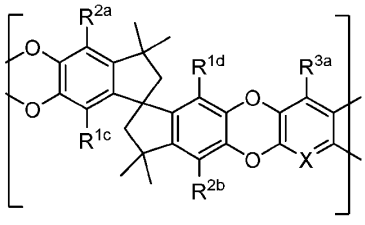
$$[A]_n\text{-}[B]_m \qquad (I) \quad ,$$

wherein each repeat unit A independently has the structure of Formula A-I:



(A-I) ,

and each repeat unit B independently have the structure of Formula B-I:



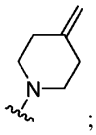
(B-I) ,

and a crosslinker,

wherein

each R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

at least two of R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are C_{2-6} alkenyl, or R^{1a1} and R^{1a2}, and R^{1b1} and R^{1b2}, are combined with the atoms to which they are attached to form:



;

R^{1c} and R^{1d} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1e}$ or $NR^{1c1}R^{1d1}$;

each R^{1c1} and R^{1d1} are independently hydrogen, C_{1-6} alkyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1c2}R^{1d2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1c2} and R^{1d2} is independently hydrogen or C_{1-6} alkyl;

each R^{1e} is independently $NR^{1c2}R^{1d2}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1f} groups;

each R^{1f} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{1f1}$, $–C(O)OR^{1f1}$, $–S(O)_2R^{1f1}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{1f1})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1f1} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CH_2R^{2c} or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{2e}$, $–C(O)OR^{2e}$, $–S(O)_2R^{2e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or $–C(R^{3b})=$;

each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or $–S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl;

subscript n is an integer from 10 to 10,000; and

subscript m is an integer from 0 to 10,000.

[0010] In another embodiment, the present invention provides a method of preparing a polymer, the method comprising: a) forming a reaction mixture comprising a cross-linkable polymer composition of the present invention, under conditions suitable to prepare the polymer.

[0011] In another embodiment, the present invention provides a separator coated with a polymer prepared by the method of the present invention.

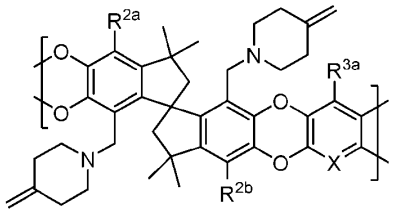
[0012] In another embodiment, the present invention provides a polymer prepared by the method of the present invention.

[0013] In another embodiment, the present invention provides an electrochemical cell comprising an anode; a cathode; a separator between the anode and cathode, wherein the separator is coated on one side with a polymer prepared by the method of the present invention; and an electrolyte composition.

[0014] In another embodiment, the present invention provides a polymer of Formula (I):

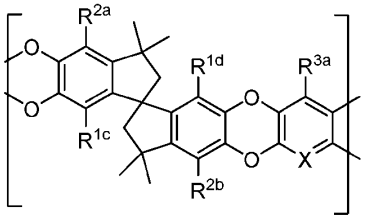
$$[A]_n\text{-}[B]_m \qquad (I) \quad ,$$

wherein each repeat unit A has the structure of Formula A-I:



(A-I) ,

and each repeat unit B independently has the structure of Formula B-I:



(B-I) ,

wherein

R^{1c} and R^{1d} are each independently hydrogen, $C_{1\text{-}6}$ alkyl, halogen, $C_{1\text{-}6}$ haloalkyl, $-CH_2R^{1e}$ or $NR^{1c1}R^{1d1}$;

each R^{1c1} and R^{1d1} are independently hydrogen, C_{1-6} alkyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1c2}R^{1d2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1c2} and R^{1d2} is independently hydrogen or C_{1-6} alkyl;

each R^{1e} is independently $NR^{1c2}R^{1d2}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1f} groups;

each R^{1f} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{1f1}$, –$C(O)OR^{1f1}$, –$S(O)_2R^{1f1}$, –C_{1-6} alkyl–(SO_3^-), –$OP(=O)(OR^{1f1})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1f1} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CH_2R^{2c} or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{2e}$, –$C(O)OR^{2e}$, –$S(O)_2R^{2e}$, –C_{1-6} alkyl–(SO_3^-), –$OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or –C(R^{3b})=;

each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or –$S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl;

subscript n is an integer from 10 to 10,000; and

subscript m is an integer from 0 to 10,000.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 shows a general crosslinking reaction scheme and examples of representative crosslinkers and representative crosslinkable molecules.

[0016] FIG. 2 shows examples of cross-linking reactions between representative crosslinkers and representative crosslinkable molecules.

[0017] FIG. 3 shows an example of a cross-linking reaction between a representative crosslinker and a representative crosslinkable molecule.

[0018] FIG. 4A and FIG. 4B shows the coated separator and multi-layer coated separator of the present invention.

[0019] FIG. 5A and FIG. 5B shows electrochemical cells of the present invention.

[0020] FIG. 6 shows the absorbance profile for solutions of PIM-13 dissolved in THF at a concentration of 6 mg/mL and exposed to four 370 nm UV lamps for a total of 60 min.

[0021] FIG. 7 shows the UV-vis absorbance spectrum for a PIM polymer, with the available lamp wavelengths, supplied by Kessel, marked with vertical lines.

DETAILED DESCRIPTION OF THE INVENTION

I. GENERAL

[0022] The present invention describes crosslinked spirobisindane polymers of intrinsic microporosity (SBI-PIMs). The cross-linked SBI-PIMs can be used in preparing coated separators which can be used in electrochemical cells. Cross-linked SBI-PIMs can provide

greater stability and lower solubility than non-crosslinked SBI-PIMs which can aid in prolonging battery lifetime and performance.

II. DEFINITIONS

[0023] The abbreviations used herein have their conventional meaning within the chemical and biological arts.

[0024] Where substituent groups are specified by their conventional chemical formulae, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, e.g., $-CH_2O-$ is equivalent to $-OCH_2-$.

[0025] "Copolymer" refers to a polymer containing at least two distinct repeat units. The two distinct repeat units can be randomly distributed in the polymer chain to form a random copolymer where the repeat units are randomly located in the polymer chain, or organized into distinct blocks of the repeat units to form a block copolymer (e.g., AAAABBBBBAAA). Copolymer also includes an alternating copolymer where the repeat units are organized in an alternating fashion in the copolymer chain: ABABABABAB.

[0026] "Molecular weight" refers to the molecular weight of the polymer as determined by Size Exclusion Chromatograph (SEC), laser-light scattering, MALDI-TOF, or other methods. The molecular weight can be measured by the weight average or the number average. "Number average molecular weight" (M_N) refers to the mole fraction of molecules in the polymer sample, i.e., the total weight of polymer divided by the total number of molecules, or the arithmetic mean. "Weight average molecular weight" (M_W) refers to the weight fraction of molecules in the polymer sample, emphasizing the weight of the individual molecules such that the M_W is greater than the M_N. The ratio of the M_W/M_N, the polydispersity index, represents the distribution of molecular weights in the polymer.

[0027] "Alkyl" refers to a straight or branched, saturated, aliphatic radical having the number of carbon atoms indicated (i.e., C_{1-6} means one to six carbons). Alkyl can include any number of carbons, such as C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{1-7}, C_{1-8}, C_{1-9}, C_{1-10}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. C_{1-6} alkyl includes, but is not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, hexyl, etc.

[0028] "Alkenyl" refers to a straight chain or branched hydrocarbon having at least 2 carbon atoms and at least one double bond and having the number of carbon atom indicated (i.e., C_{2-6} means to two to six carbons). Alkenyl can include any number of carbons, such as C_2, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{2-7}, C_{2-8}, C_{2-9}, C_{2-10}, C_3, C_{3-4}, C_{3-5}, C_{3-6}, C_4, C_{4-5}, C_{4-5}, C_5, C_{5-6}, and C_6. Alkenyl groups can have any suitable number of double bonds, including, but not limited to, 1, 2, 3, 4, 5 or more. Examples of C_{2-4} alkenyl groups include, but are not limited to, vinyl (ethenyl), propenyl, isopropenyl, 1-butenyl, 2-butenyl, isobutenyl, or butadienyl.

[0029] "Alkynyl" refers to either a straight chain or branched hydrocarbon having at least 2 carbon atoms and at least one triple bond and having the number of carbon atom indicated (i.e., C_{2-6} means to two to six carbons). Alkynyl can include any number of carbons, such as C_2, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{2-7}, C_{2-8}, C_{2-9}, C_{2-10}, C_3, C_{3-4}, C_{3-5}, C_{3-6}, C_4, C_{4-5}, C_{4-6}, C_5, C_{5-6}, and C_6. Examples of C_{2-4} alkynyl groups include, but are not limited to, acetylenyl, propynyl, 1-butynyl, 2-butynyl, isobutynyl, sec-butynyl, or butadiynyl.

[0030] "Hydroxyalkyl" or "alkylhydroxy" refers to an alkyl group, as defined above, where at least one of the hydrogen atoms is replaced with a hydroxy group. As for the alkyl group, hydroxyalkyl or alkylhydroxy groups can have any suitable number of carbon atoms, such as C_{1-6}. Exemplary C_{1-4} hydroxyalkyl groups include, but are not limited to, hydroxymethyl, hydroxyethyl (where the hydroxy is in the 1- or 2-position), hydroxypropyl (where the hydroxy is in the 1-, 2- or 3-position), hydroxybutyl (where the hydroxy is in the 1-, 2-, 3- or 4-position), 1,2-dihydroxyethyl, and the like.

[0031] "Alkyl-Alkoxy" or "alkoxyalkyl" refers to a radical having an alkyl component and an alkoxy component, where the alkyl component links the alkoxy component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the alkoxy component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The alkoxy component is as defined above. Examples of the alkyl-alkoxy group include, but are not limited to, 2-ethoxy-ethyl and methoxymethyl.

[0032] "Halogen" refers to fluorine, chlorine, bromine and iodine.

[0033] "Haloalkyl" refers to alkyl, as defined above, where some or all of the hydrogen atoms are replaced with halogen atoms. As for alkyl group, haloalkyl groups can have any suitable number of carbon atoms, such as C_{1-6}. For example, haloalkyl includes

trifluoromethyl, fluoromethyl, 2,2,2-trifluoroethyl, etc. In some instances, haloalkyl includes the term "fluoroalkyl" that can be used to define an alkyl group where one or more hydrogen is replaced with fluorine.

[0034] "Cycloalkyl" refers to a saturated or partially unsaturated, monocyclic, fused bicyclic or bridged polycyclic ring assembly containing from 3 to 12 ring atoms, or the number of atoms indicated. Cycloalkyl can include any number of carbons, such as C_{3-6}, C_{4-6}, C_{5-6}, C_{3-8}, C_{4-8}, C_{5-8}, C_{6-8}, C_{3-9}, C_{3-10}, C_{3-11}, and C_{3-12}. Saturated monocyclic cycloalkyl rings include, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cyclooctyl. Saturated bicyclic and polycyclic cycloalkyl rings include, for example, norbornane, [2.2.2] bicyclooctane, decahydronaphthalene and adamantane. Cycloalkyl groups can also be partially unsaturated, having one or more double or triple bonds in the ring. Representative cycloalkyl groups that are partially unsaturated include, but are not limited to, cyclobutene, cyclopentene, cyclohexene, cyclohexadiene (1,3- and 1,4-isomers), cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene (1,3-, 1,4- and 1,5-isomers), norbornene, and norbornadiene. When cycloalkyl is a saturated monocyclic C_{3-8} cycloalkyl, exemplary groups include, but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. When cycloalkyl is a saturated monocyclic C_{3-6} cycloalkyl, exemplary groups include, but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Cycloalkyl groups can be substituted or unsubstituted.

[0035] "Alkyl-cycloalkyl" refers to a radical having an alkyl component and a cycloalkyl component, where the alkyl component links the cycloalkyl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the cycloalkyl component and to the point of attachment. In some instances, the alkyl component can be absent. The alkyl component can include any number of carbons, such as C_{1-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. The cycloalkyl component is as defined within. Exemplary alkyl-cycloalkyl groups include, but are not limited to, methyl-cyclopropyl, methyl-cyclobutyl, methyl-cyclopentyl and methyl-cyclohexyl.

[0036] "Heterocycle" or "heterocycloalkyl" refers to a saturated ring system having from 3 to 12 ring members and from 1 to 4 heteroatoms of N, O and S. The heteroatoms can also be oxidized, such as, but not limited to, -S(O)- and $-S(O)_2-$. Heterocycloalkyl groups can include any number of ring atoms, such as, 3 to 6, 4 to 6, 5 to 6, 3 to 8, 4 to 8, 5 to 8, 6 to 8, 3

to 9, 3 to 10, 3 to 11, or 3 to 12 ring members. Any suitable number of heteroatoms can be included in the heterocycloalkyl groups, such as 1, 2, 3, or 4, or 1 to 2, 1 to 3, 1 to 4, 2 to 3, 2 to 4, or 3 to 4. The heterocycloalkyl group can include groups such as aziridine, azetidine, pyrrolidine, piperidine, azepane, azocane, quinuclidine, pyrazolidine, imidazolidine, piperazine (1,2-, 1,3- and 1,4-isomers), oxirane, oxetane, tetrahydrofuran, oxane (tetrahydropyran), oxepane, thiirane, thietane, thiolane (tetrahydrothiophene), thiane (tetrahydrothiopyran), oxazolidine, isoxazolidine, thiazolidine, isothiazolidine, dioxolane, dithiolane, morpholine, thiomorpholine, dioxane, or dithiane. The heterocycloalkyl groups can also be fused to aromatic or non-aromatic ring systems to form members including, but not limited to, indoline. Heterocycloalkyl groups can be unsubstituted or substituted. For example, heterocycloalkyl groups can be substituted with C_{1-6} alkyl or oxo (=O), among many others.

[0037] "Alkyl-heterocycloalkyl" refers to a radical having an alkyl component and a heterocycloalkyl component, where the alkyl component links the heterocycloalkyl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the heterocycloalkyl component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The heterocycloalkyl component is as defined above. Alkyl-heterocycloalkyl groups can be substituted or unsubstituted.

[0038] "Aryl" refers to an aromatic ring system having any suitable number of ring atoms and any suitable number of rings. Aryl groups can include any suitable number of ring atoms, such as, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16 ring atoms, as well as from 6 to 10, 6 to 12, or 6 to 14 ring members. Aryl groups can be monocyclic, fused to form bicyclic or tricyclic groups, or linked by a bond to form a biaryl group. Representative aryl groups include phenyl, naphthyl and biphenyl. Other aryl groups include benzyl, having a methylene linking group. Some aryl groups have from 6 to 12 ring members, such as phenyl, naphthyl or biphenyl. Other aryl groups have from 6 to 10 ring members, such as phenyl or naphthyl. Some other aryl groups have 6 ring members, such as phenyl. Aryl groups can be substituted or unsubstituted.

[0039] "Alkyl-aryl" refers to a radical having an alkyl component and an aryl component, where the alkyl component links the aryl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the aryl component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The aryl component is as defined above. Examples of alkyl-aryl groups include, but are not limited to, benzyl and ethyl-benzene. Alkyl-aryl groups can be substituted or unsubstituted.

[0040] "Heteroaryl" refers to a monocyclic or fused bicyclic or tricyclic aromatic ring assembly containing 5 to 16 ring atoms, where from 1 to 5 of the ring atoms are a heteroatom such as N, O or S. The heteroatoms can also be oxidized, such as, but not limited to, N-oxide, -S(O)- and $-S(O)_2-$. The nitrogen atom(s) can also be quaternized. Heteroaryl groups can include any number of ring atoms, such as, 5 to 6, 5 to 8, 6 to 8, 5 to 9, 5 to 10, 5 to 11, or 5 to 12 ring members. Any suitable number of heteroatoms can be included in the heteroaryl groups, such as 1, 2, 3, 4, or 5, or 1 to 2, 1 to 3, 1 to 4, 1 to 5, 2 to 3, 2 to 4, 2 to 5, 3 to 4, or 3 to 5. Heteroaryl groups can have from 5 to 10 ring members and from 1 to 4 heteroatoms, from 5 to 8 ring members and from 1 to 4 heteroatoms, or from 5 to 8 ring members and from 1 to 3 heteroatoms, or from 5 to 6 ring members and from 1 to 4 heteroatoms, or from 5 to 6 ring members and from 1 to 3 heteroatoms. The heteroaryl group can include groups such as pyrrole, pyridine, imidazole, pyrazole, triazole, tetrazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiophene, furan, thiazole, isothiazole, oxazole, and isoxazole. The heteroaryl groups can also be fused to aromatic ring systems, such as a phenyl ring, to form members including, but not limited to, benzopyrroles such as indole and isoindole, benzopyridines such as quinoline and isoquinoline, benzopyrazine (quinoxaline), benzopyrimidine (quinazoline), benzopyridazines such as phthalazine and cinnoline, benzothiophene, and benzofuran. Other heteroaryl groups include heteroaryl rings linked by a bond, such as bipyridine.

[0041] The heteroaryl groups can be linked via any position on the ring. For example, pyrrole includes 1-, 2- and 3-pyrrole, pyridine includes 2-, 3- and 4-pyridine, imidazole includes 1-, 2-, 4- and 5-imidazole, pyrazole includes 1-, 3-, 4- and 5-pyrazole, triazole includes 1-, 4- and 5-triazole, tetrazole includes 1- and 5-tetrazole, pyrimidine includes 2-, 4-, 5- and 6- pyrimidine, pyridazine includes 3- and 4-pyridazine, 1,2,3-triazine includes 4- and

5-triazine, 1,2,4-triazine includes 3-, 5- and 6-triazine, 1,3,5-triazine includes 2-triazine, thiophene includes 2- and 3-thiophene, furan includes 2- and 3-furan, thiazole includes 2-, 4- and 5-thiazole, isothiazole includes 3-, 4- and 5-isothiazole, oxazole includes 2-, 4- and 5-oxazole, isoxazole includes 3-, 4- and 5-isoxazole, indole includes 1-, 2- and 3-indole, isoindole includes 1- and 2-isoindole, quinoline includes 2-, 3- and 4-quinoline, isoquinoline includes 1-, 3- and 4-isoquinoline, quinazoline includes 2- and 4-quinoazoline, cinnoline includes 3- and 4-cinnoline, benzothiophene includes 2- and 3-benzothiophene, and benzofuran includes 2- and 3-benzofuran.

[0042] Some heteroaryl groups include those having from 5 to 10 ring members and from 1 to 3 ring atoms including N, O or S, such as pyrrole, pyridine, imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiophene, furan, thiazole, isothiazole, oxazole, isoxazole, indole, isoindole, quinoline, isoquinoline, quinoxaline, quinazoline, phthalazine, cinnoline, benzothiophene, and benzofuran. Other heteroaryl groups include those having from 5 to 8 ring members and from 1 to 3 heteroatoms, such as pyrrole, pyridine, imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiophene, furan, thiazole, isothiazole, oxazole, and isoxazole. Some other heteroaryl groups include those having from 9 to 12 ring members and from 1 to 3 heteroatoms, such as indole, isoindole, quinoline, isoquinoline, quinoxaline, quinazoline, phthalazine, cinnoline, benzothiophene, benzofuran and bipyridine. Still other heteroaryl groups include those having from 5 to 6 ring members and from 1 to 2 ring atoms including N, O or S, such as pyrrole, pyridine, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, thiophene, furan, thiazole, isothiazole, oxazole, and isoxazole.

[0043] Some heteroaryl groups include from 5 to 10 ring members and only nitrogen heteroatoms, such as pyrrole, pyridine, imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), indole, isoindole, quinoline, isoquinoline, quinoxaline, quinazoline, phthalazine, and cinnoline. Other heteroaryl groups include from 5 to 10 ring members and only oxygen heteroatoms, such as furan and benzofuran. Some other heteroaryl groups include from 5 to 10 ring members and only sulfur heteroatoms, such as thiophene and benzothiophene. Still other heteroaryl groups include from 5 to 10 ring members and at least two heteroatoms, such as imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiazole, isothiazole, oxazole, isoxazole, quinoxaline, quinazoline, phthalazine, and cinnoline.

[0044] "Alkyl-heteroaryl" refers to a radical having an alkyl component and a heteroaryl component, where the alkyl component links the heteroaryl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the heteroaryl component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The heteroaryl component is as defined within. Alkyl-heteroaryl groups can be substituted or unsubstituted.

[0045] "Salt" refers to acid or base salts of the compounds used in the methods of the present invention. Salts of the basic compounds of the present invention are salts formed with acids, such as mineral acids, organic carboxylic, and organic sulfonic acids. Namely examples of salts include, but are not limited to, halogen salts, such as fluoride, chloride, bromide, and iodide salts, oxanion salts, such as chlorate, bromate, iodate, carbonate, nitrate, sulfate, or phosphate salts, carboxylic salts, such as fumerate or acetate salts, and sulfonate salts, such as trifluoromethylsulfonate salts

[0046] Also included are base addition salts such as sodium, potassium, calcium, ammonium, organic amino, or magnesium salt, or a similar salt, provided an acidic group constitutes part of the structure. Illustrative examples of salts are mineral acid (hydrochloric acid, hydrobromic acid, phosphoric acid, and the like) salts, organic acid (acetic acid, propionic acid, glutamic acid, citric acid and the like) salts, quaternary ammonium (methyl iodide, ethyl iodide, and the like) salts.

[0047] "Sulfonate" refers to a compound comprising $-S(O)_3^-$. Examples of sulfonates include, but are not limited to, $H_3C-S(O)_3^-$, $H_3CCH_2-S(O)_3^-$, or $F_3C-S(O)_3^-$. Sulfonates can include any chemical group attached to $-S(O)_3^-$ by a single bond.

[0048] "Carbonate" refers to a compound of the formula R'OC(O)OR", where R' and R" can be the same or different, or combined to form a cyclic structure. R' and R" can be alkyl, haloalkyl, or combined to form an alkylene that is optionally substituted with halogen. Representative carbonates include, but are not limited to, dimethyl carbonate and fluoroethylene carbonate.

[0049] "Forming a reaction mixture" refers to the process of bringing into contact at least two distinct species such that they mix together and can react. It should be appreciated, however, that the resulting reaction product can be produced directly from a reaction between

the added reagents or from an intermediate from one or more of the added reagents which can be produced in the reaction mixture.

[0050] "Crosslinker" refers to a compound comprising one or more reactive functional groups that can react with one or more crosslinkable molecules to form a product connecting the crosslinker and the one or more crosslinkable molecules. A crosslinkable molecule refers to a molecule that can react with a crosslinker to form a product. Without being bound by any particular theory, the reaction between the crosslinker and the one or more crosslinkable molecules to form a product connecting the crosslinker and the one or more crosslinkable molecules can be initiated by heat, light, catalyst, or any suitable trigger. The one or more reactive functional groups of the crosslinker can be nucleophilic or electrophilic. The one or more crosslinkable molecules to be connected by the crosslinker can be polymers. Representative reactive functional groups for crosslinkers include, but are not limited to, hydroxyls, amines, thiols, epoxides, isocyanates, alkyl halides, and alkenes. Other crosslinkers and reactive functional groups are useful in the present invention.

[0051] "Solvent" refers to a substance, such as a liquid, capable of dissolving a solute. Solvents can be polar or non-polar, protic or aprotic. Polar solvents typically have a dielectric constant greater than about 5 or a dipole moment below about 1.0. Protic solvents are characterized by having a proton available for removal, such as by having a hydroxyl or carboxy group. Aprotic solvents lack such a group. Representative polar protic solvents include alcohols (methanol, ethanol, propanol, isopropanol, etc.), acids (formic acid, acetic acid, etc.) and water. Representative polar aprotic solvents include dichloromethane, chloroform, tetrahydrofuran, diethyl ether, acetone, ethyl acetate, dimethylformamide, dimethylacetamide, acetonitrile, and dimethyl sulfoxide. Representative non-polar solvents include alkanes (pentanes, hexanes, etc.), benzene, toluene, and 1,4-dioxane. Other solvents are useful in the present invention.

[0052] "Thiol" refers to a compound comprising a sulfhydryl group, –SH. Thiols can include any chemical group attached to –SH by a single bond and can comprise more than one –SH group per molecule. Examples of thiols include, but are not limited to, 1-octanethiol, thiophenol, 2,2'-(ethylenedioxy)diethanethiol, and trimethylolpropane tris(3-mercaptopropionate). Other thiols, including thiols with multiple –SH groups per molecule, are useful in the present invention.

[0053] "Photointiator" refers to a compound that generates a reactive species upon light absorption. Without being bound by any particular theory, the reactive species generated from a photointiator can promote chemical reactions, including a crosslinking reaction. Representative photointiators include benzophenone, benzil, acetophenone, and anthraquinone. Other photointiators are useful in the present invention.

[0054] "Crosslinking additive" refers to one or more compounds added to a reaction capable of reacting with the crosslinker. The crosslinking additive can be, but is not limited to, an additional crosslinker or can support lithium transport.

[0055] "Alkyl acrylate" refers to a compound of the formula CH=CHC(O)OR, where R is alkyl or cycloalkyl, as defined above.

[0056] "Fluoroalkyl acrylate" refers to an alkyl acrylate, as defined above, where some or all of the hydrogen atoms of the R group are replaced with fluorine atoms.

[0057] "Irradiation" refers to a process of exposing a molecule, reaction mixture, or other composition to radiation. Radiation includes, but is not limited to, ultraviolet (UV) light. UV light includes a wavelength less than 400 nm. Exposing a molecule, reaction mixture, or other composition with UV light over a given period of time provides a UV dose. A UV dose (mJ/cm^2) is calculated by multiplying the intensity of the UV light (mW/cm^2) × the exposure time (s). Any suitable UV dose up to 10,000 mJ/cm^2 can be useful in the present invention.

[0058] "Curing" refers to a chemical or physical change in a molecule induced by irradiation, heat, catalyst, or by some other process. A physical change in the molecule can be polymerization or hardening.

[0059] "Electrode" refers to an electrically conductive material in a circuit that is in contact with a nonmetallic part of the circuit, such as the electrolyte. The electrode can be a positive electrode or cathode, the electrode where reduction occurs. The electrode can be a negative electrode or anode, the electrode where oxidation occurs.

[0060] "Anode" refers to a negative electrode, as described above.

[0061] "Cathode" refers to a positive electrode, as described above.

[0062] "Electrolyte" refers to a solution of the electrochemical cell that includes ions, such as metal ions and protons as well as anions, that provides ionic communication between the positive and negative electrodes.

[0063] "Electrolyte solvent" refers to the molecules solvating ions in the liquid electrolyte, such as small organic carbonates or ethereal molecules, that enable diffusion of ions in the electrolyte. The electrolyte solvent may also be an ionic liquid or a gas at standard temperature and pressure.

[0064] "Separator" refers to an electrically insulating membrane between the positive and negative electrodes to prevent electrical shorts, i.e., provides electronic isolation. The separator also allows the ions to move between the positive and anode electrodes. The separator can include any suitable polymeric or inorganic material that is electrically insulating. The separator can include several layers including one or more membrane layers, and a porous support material for the membrane layers.

[0065] "First polymer layer" refers to a layer of the separator that is permeable to a first species of the electrolyte while substantially impermeable to liquid electrolyte. The membrane layer can be of any suitable material that can provide the selective permeability, such as composites of microporous polymers and inorganic materials. "Substantially impermeable" refers to less than 10% of the electrolyte solvent passing through the membrane layer, or less than 1%, or less than 0.1%, or less than 0.01%, or less than 0.001% of the liquid electrolyte passing through the membrane layer.

[0066] "Oxide" refers to a chemical compound having an oxygen, such as metal oxides or molecular oxides.

[0067] "Pore size" or "pore diameter" refers to the average diameter of interstitial space not occupied by the pore forming material. This may include, but is not limited to, the space remaining between polymer chains due to inefficient packing, the space remaining between organic linkers and metal ions in a metal-organic framework, the space between layers and within the holes of stacked 2D material, and the space left in an amorphous or semi-crystalline carbon due to unaligned covalent bonding. The pore size may also change once wetted with electrolyte or it may stay the same.

[0068] "Surface area" refers to the surface area of a porous material as measured by a variety of methods, such as nitrogen adsorption BET.

[0069] "Microporous polymer" refers to an amorphous glassy polymer having interconnected pores with an average diameter of less than 10 nm, or less than 5, 4, 3, 2, or less than 1 nm.

[0070] "Microporosity" refers to a layer of the membrane comprising pores of less than or equal to 2 nm in size.

[0071] "Intrinsic microporosity" refers to a polymer providing a continuous network of interconnected intermolecular voids (suitably of less than or equal to 4 nm in size), which forms as a direct consequence of the shape and rigidity of at least a proportion of the component monomers of the polymer. As will be appreciated by a person skilled in the art, intrinsic microporosity arises due to the structure of the monomers used to form the polymer and, as the term suggests, it is an intrinsic property of a polymer formed from such monomers.

[0072] It is understood that the network polymers disclosed herein have a certain property (i.e. intrinsic microporosity). Disclosed herein are certain structural requirements in the monomers used for giving a polymer performing the disclosed function, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed monomer structures, and that these structures will typically achieve the same result.

[0073] "Metal" refers to elements of the periodic table that are metallic and that can be neutral, or negatively or positively charged as a result of having more or fewer electrons in the valence shell than is present for the neutral metallic element. Metals useful in the present invention include the alkali metals, alkali earth metals, transition metals and post-transition metals. Alkali metals include Li, Na, K, Rb and Cs. Alkaline earth metals include Be, Mg, Ca, Sr and Ba. Transition metals include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg and Ac. Post-transition metals include Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, and Po. Rare earth metals include Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. One of skill in the art will appreciate that the metals described above can each adopt several different oxidation states, all of which are useful in the present invention. In some instances, the most stable oxidation state is formed, but other oxidation states are useful in the present invention.

[0074] "Porous support" refers to any suitable material that is capable of supporting the membrane layer of the present invention, and is permeable to the electrolyte.

[0075] "Laminated" refers to the deposition of one layer on another, such as the microporous polymer layer or first polymer layer onto the porous support.

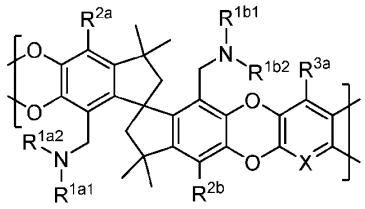
III. CROSS-LINKABLE POLYMER COMPOSITION

[0076] In some embodiments, the present invention provides a cross-linkable polymer composition comprising:

a polymer of Formula (I):

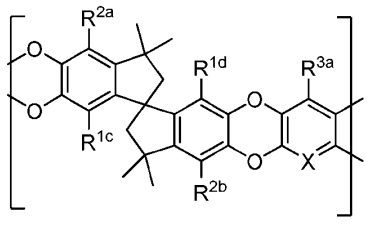
$$[A]_n\text{-}[B]_m \quad (I) \quad ,$$

wherein each repeat unit A independently has the structure of Formula A-I:



(A-I) ,

and each repeat unit B independently have the structure of Formula B-I:



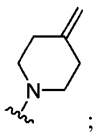
(B-I) ,

and a crosslinker,

wherein

each R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

at least two of R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are C_{2-6} alkenyl, or R^{1a1} and R^{1a2}, and R^{1b1} and R^{1b2}, are combined with the atoms to which they are attached to form:



;

R^{1c} and R^{1d} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1e}$ or $NR^{1c1}R^{1d1}$;

each R^{1c1} and R^{1d1} are independently hydrogen, C_{1-6} alkyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1c2}R^{1d2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1c2} and R^{1d2} is independently hydrogen or C_{1-6} alkyl;

each R^{1e} is independently $NR^{1c2}R^{1d2}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1f} groups;

each R^{1f} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{1f1}$, –$C(O)OR^{1f1}$, –$S(O)_2R^{1f1}$, –C_{1-6} alkyl–(SO_3^-), –$OP(=O)(OR^{1f1})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1f1} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CH_2R^{2c} or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{2e}$, –$C(O)OR^{2e}$, –$S(O)_2R^{2e}$, –C_{1-6} alkyl–(SO_3^-), –$OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or –C(R^{3b})=;

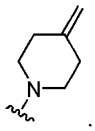
each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or –$S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl;

subscript n is an integer from 10 to 10,000; and

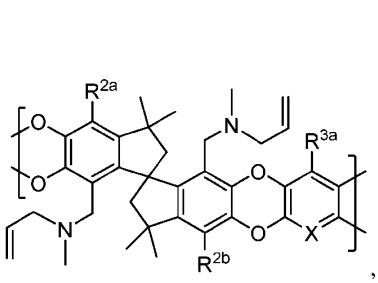
subscript m is an integer from 0 to 10,000.

[0077] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein each R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are independently C_{1-6} alkyl, or C_{2-6} alkenyl; and at least one of R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} is C_{2-6} alkenyl, or R^{1a1} and R^{1a2}, and R^{1b1} and R^{1b2}, are combined with the atoms to which they are attached to form:

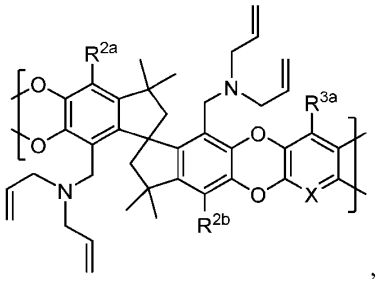


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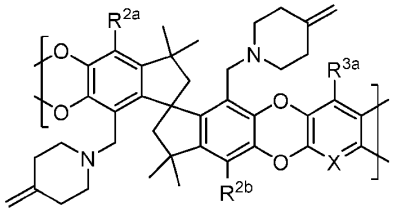
[0078] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein each repeat unit A independently has the structure:



,



, or

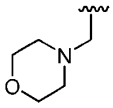


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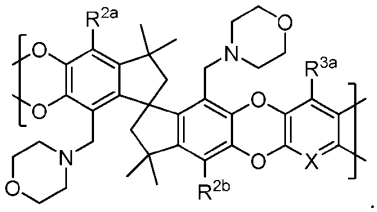
[0079] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein subscript m is 0. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein subscript

m is an integer from 10 to 10,000. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein subscript m is an integer from 10 to 1,000.

[0080] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein R^{1c} and R^{1d} are each independently–CH_2R^{1e}; and each R^{1e} is independently a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein R^{1c} and R^{1d} are each



[0081] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein each repeat unit B independently has the structure:



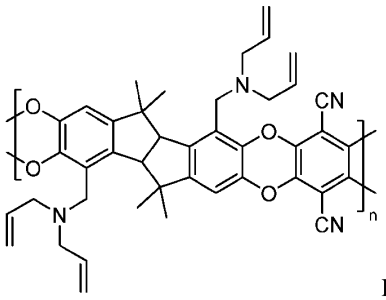
[0082] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the molar ratio of repeat unit A to repeat unit B is from about 10:90 to about 99:1, or about 20:80 to about 98:2, about 25:75 to about 98:2, about 30:70 to about 97.5:2.5, about 50:50 to about 97.5:2.5, about 50:50 to about 95:5, or about 50:50 to about 90:10. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the molar ratio of repeat unit A to repeat unit B is about 99:1, or about 98.5:1.5, 98:2, 97.5:2.5, 97:3, 96.5:3.5, 96:4, 95.5:4.5, 95:5, 94:6, 93:7, 92:8, 91:9, 90:10, 87.5:12.5, 85:15, 82.5:17.5, 80:20, 75:25, 70:30, 65:35, 60:40, 55:45, 50:50, 45:55, 40:60, 35:65, 30:70, 25:75, 20:80, 15:85, 10:90, 5:95, or about 1:99. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the molar ratio of repeat unit A to repeat unit B is 5:95, 10:90, 15:85, 20:80, 25:75, 30:70, 35:65, 40:60, 45:55, 50:50, 55:45, 60:40, 65:45, 70:30, 75:25, 80:20, 85:15, 90:10, or 95:5. In some embodiments, the cross-linkable polymer composition of the

present invention is the composition wherein the ratio of repeat unit A to repeat unit B is 50:50.

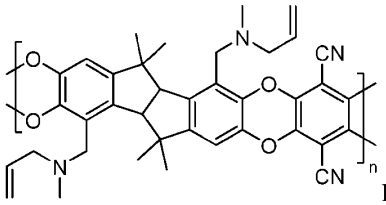
[0083] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein R^{2a} and R^{2b} are each hydrogen.

[0084] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein R^{3a} is –CN, X is $-C(R^{3b})=$, and R^{3b} is –CN.

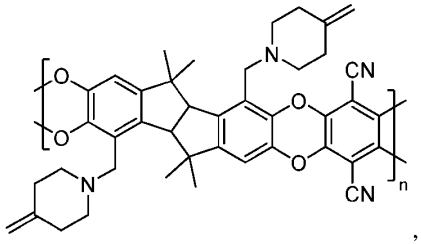
[0085] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is:



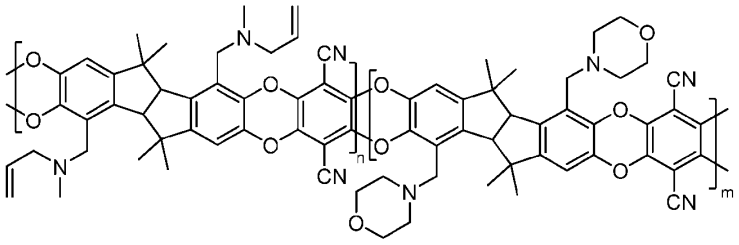
PIM-DAA,



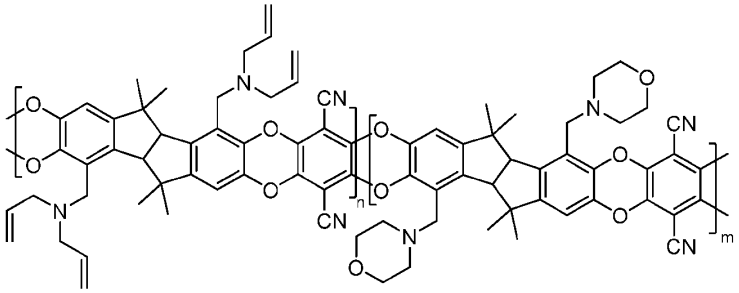
PIM-MAA,



,



PIM-13/PIM-MAA, or



PIM-13/PIM-DAA.

[0086] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from 1 kg/mol to 1000 kg/mol, or 1 kDa to 1000 kDa. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from 10 kg/mol to 500 kg/mol, or from 20 kg/mol to 400 kg/mol, or from 30 kg/mol to 300 kg/mol, or from 40 kg/mol to 200 kg/mol, or from 50 kg/mol to 175 kg/mol, or from 50 kg/mol to 150 kg/mol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from 1 kg/mol to 1000 kg/mol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from 10 kg/mol to 500 kg/mol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from 35 kg/mol to 250 kg/mol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from 55 kg/mol to 150 kg/mol. The molecular weight of the polymer of Formula (I) can be calculated by a variety of

methods including, but not limited to, size exclusion chromatography (SEC), laser light scattering, MALDI-TOF, and others. Molecular weight determination of the polymers in the present invention is made using a Waters APC SEC (Size Exclusion Chromatograph) system with RI detector compared against polystyrene standards for relative molecular weight, or a Malvern OMNISEC GPC with triple detector for absolute molecular weight determination.

[0087] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker comprises a thiol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is a dithiol, trithiol, tetrathiol, pentathiol, or hexathiol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is 2,2'-(ethylenedioxy)diethanethiol, trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerithritol hexakis(3-mercaptopropionate), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate, dipentaerythritol hexakis(3-mercaptopropionate), hexa(ethylene glycol) dithiol, 1,11-dimercapto-3,6,9-trioxaundecane, cyclohexane-1,4-diyl bis(3-mercaptopropanoate), di(ethylene glycol) bis(3-mercaptopropionate), tri(ethylene glycol) bis(3-mercaptopropionate), or tetra(ethylene glycol) bis(3-mercaptopropionate). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is 2,2'-(ethylenedioxy)diethanethiol, trimethylolpropane tris(3-mercaptopropionate), or pentaerythritol tetrakis(3-mercaptopropionate). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is 2,2'-(ethylenedioxy)diethanethiol. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is trimethylolpropane tris(3-mercaptopropionate). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is pentaerythritol tetrakis(3-mercaptopropionate).

[0088] Additional components of the cross-linkable polymer composition can include crosslinkers defined by their structure or functional groups, such as the number of carbon atoms in the molecular chain, the presence of branching, or other functional groups that facilitate crosslinking, including but not limited to alkene, epoxy, or isocyanate groups.

[0089] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is present in an amount of from about 5

to 90 mol% relative to the polymer of Formula (I). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is present in an amount of from about 5 to 75 mol% relative to the polymer of Formula (I). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is present in an amount of from about 12.5 to 50 mol% relative to the polymer of Formula (I). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinker is present in an amount of about 12.5, 25, or 50 mol% relative to the polymer of Formula (I).

[0090] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the reaction mixture further comprises a solvent. . In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the solvent comprises water, methanol, ethanol, propanol, isopropanol, dichloromethane, chloroform, 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran, 2-methyl tetrahydrofuran diethyl ether, dimethoxy ethane, diisopropyl ether, N-methylpyrrolidone, or a combination thereof. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the solvent comprises water, 1,3-dioxolane, tetrahydrofuran, or N-methylpyrrolidone, or a combination thereof. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the solvent is 1,3-dioxolane.

[0091] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) and crosslinker are at a concentration of from about 10 to 100 mL/mL in the solvent. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) and crosslinker are at a concentration of from 10 to 100 mL/mL in the solvent, or from 20 to 90 mL/mL, or from 30 to 80 mL/mL, or from 40 to 70 mL/mL, or from 50 to 60 mL/mL. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) and crosslinker are at a concentration of about 60 mL/mL in the solvent.

[0092] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the reaction mixture further comprises a photointiator. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the photoinitiator comprises acetophenone, anisoin, anthraquinone,

anthraquinone-2-sulfonic acid sodium salt monohydrate, benzil, benzoin, benzoin ethyl ether, benzoin isobutyl ether, benzophenone, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4-benzoylbiphenyl, 2-benzyl-2-(dimethylamino)-4'- morpholinobutyrophenone, 4,4'-bis(diethylamino)benzophenone, 4,4'-bis(dimethylamino)benzophenone, camphorquinone, 2-chlorothioxanthen-9-one, (cumene)cyclopentadienyliron(II) hexafluorophosphate, dibenzosuberenone, 2,2-diethoxyacetophenone, 4,4'-dihydroxybenzophenone, 2,2-dimethoxy-2-phenylacetophenone (DMPA), 4-(dimethylamino)benzophenone, 4,4'-dimethylbenzil, 2,5-dimethylbenzophenone, 3,4-dimethylbenzophenone, diphenyl(2,4,6 trimethylbenzoyl)phosphine oxide, 4'-ethoxyacetophenone, ethylanthraquinone, ferrocene, 3'-hydroxyacetophenone, 4'-hydroxyacetophenone, 3-hydroxybenzophenone, 4-hydroxybenzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methylpropiophenone, 4-hydroxybenzophenone, 3-methylbenzophenone, methyl benzoylformate, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, phenanthrenequinone, 4'-phenoxyacetophenone, or a combination thereof. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA).

[0093] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the reaction mixture further comprises a crosslinking additive. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinking additive comprises alkyl acrylate, methyl acrylate, pentaerythritol tetraacrylate, trimethylolpropane triacrylate, 2,2,2-trifluoroethyl acrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate, fluoroalkyl acrylate, pentafluorophenyl acrylate, 2-(dimethylamino)ethyl acrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-isocyanatoethyl acrylate, tetrahydrofurfuryl acrylate, 4-acryloylmorpholine, triisopropylsilyl acrylate, 3-[dimethyoxy(methyl)silyl]propyl acrylate, 3-(methoxydimethylsilyl)propyl acrylate, 3-(trimethoxysilyl)propyl acrylate, *N*-succinimidyl acrylate, 2-cyanoethyl acrylate, α-methylene-γ-butyrolactone, (diethoxyphosphoryl)methyl acrylate, oxiran-2-ylmethyl acrylate, 4-hydroxybutyl acrylate glycidyl ether, 2-*N*-morpholinoethyl acrylate, *N*,*N*-dimethylprop-2-en-1-amine, acrylamide, *N*-(isobutoxymethyl)acrylamide, *N*-(2-(pyridin-2-yl)ethyl)acrylamide, *N*-[3-dimethylamino)propyl]methacrylamide, *N*-[2-(dimethylamino)ethyl]methacrylamide, *N*-[3-(dimethylamino)propyl]acrylamide, 2-(diethylamino)ethyl methacrylate, *N*-[2-(5-imidazolyl)ethyl]acrylamide, 1-vinylimidazole, 1-vinyl-1,2,4-triazole, 2-methyl-1-

vinylimidazole, 4-vinylpyridine, styrene, 4-(trifluoromethyl)styrene, 4-methoxystyrene, 4-(trifluoromethoxy)styrene, alpha-(trifluoromethyl)styrene, 3,5-bis(trifluoromethyl)styrene, or a combination thereof. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the crosslinking additive is pentaerythritol tetraacrylate, trimethylolpropane triacrylate, 4-acryloylmorpholine, *N*,*N*-dimethylprop-2-en-1-amine, or 1-vinylimidazole.

[0094] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-DAA, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 12.5 mol% relative to PIM-DAA, and the solvent is 1,3-dioxolane. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-MAA, the crosslinker is trimethylolpropane tris(3-mercaptopropionate) and is present in an amount of about 25 mol% relative to PIM-DAA, and the solvent is 1,3-dioxolane. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-13/PIM-MAA (50/50) copolymer, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 25 mol% relative to PIM-13/PIM-MAA (50/50), and the solvent is 1,3-dioxolane. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-13/PIM-DAA (10/90) copolymer, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 50 mol% relative to PIM-13/PIM-DAA (10/90), the solvent is 1,3-dioxolane, and the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) and is present in an amount of about 2.5 mol% relative to PIM-13/PIM-DAA (10/90). In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-13/PIM-DAA (20/80) copolymer, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 50 mol% relative to PIM-13/PIM-DAA (20/80), and the solvent is 1,3-dioxolane. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-13/PIM-DAA (30/70) copolymer, the crosslinker is trimethylolpropane tris(3-mercaptopropionate) and is present in an amount of about 30 mol% relative to PIM-13/PIM-DAA (30/70), the solvent is 1,3-dioxolane, and the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) and is present in an amount of about 5 mol% relative to PIM-13/PIM-DAA (30/70). In some embodiments, the cross-

linkable polymer composition of the present invention is the composition wherein the polymer of Formula (I) is PIM-13/PIM-DAA (50/50) copolymer, the crosslinker is tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate and is present in an amount of about 25 mol% relative to PIM-13/PIM-DAA (50/50), the solvent is 1,3-dioxolane, and the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) present in an amount of about 2.5 mol% relative to PIM-13/PIM-DAA (50/50).

[0095] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the reaction mixture further comprises a filler.

[0096] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the filler comprises an inorganic particle. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the inorganic particle comprises boehmite (γ-AlOOH), alumina (Al_2O_3), barium sulfate ($BaSO_4$), magnesium oxide (MgO), magnesium hydroxide ($Mg(OH)_2$), silicon dioxide (SiO_2), tin dioxide (SnO_2), titanium oxide (TiO_2), calcium oxide (CaO), zinc oxide (ZnO), zirconia (ZrO_2), yttrium oxide (Y_2O_3), nickel oxide (NiO), cerium oxide (CeO_2), zirconium titanate ($SrTiO_3$), barium titanate ($BaTiO_3$), and magnesium fluorine (MgF_2), or a combination thereof. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the inorganic particle is present in an amount of from about 0.1 to 20 wt% relative to the weight of the polymer of Formula (I).

[0097] In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the filler comprises a nanoparticle. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the nanoparticle comprises graphene oxide, reduced graphene oxide, boron nitride (BN), silicon nitride (Si_3N_4), silicon carbide (SiC), silicon (Si), lithium lanthanum zirconium oxide (LLZO), tetraboron carbide (B_4C), silicon dioxide (SiO_2), silicon disulfide (SiS_2), phosphorus pentasulfide (P_2S_5), zirconium dioxide (ZrO_2), aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), tin dioxide (SnO_2), cerium dioxide (CeO_2), magnesium oxide (MgO), nickel oxide (NiO), zinc oxide (ZnO), zinc trioxide (ZnO_3), aluminum monoxide (AlO), lithium phosphate (Li_3PO_4), or a combination thereof. In some embodiments, the cross-linkable polymer composition of the present invention is the composition wherein the inorganic particle is present in an amount of from about 0.1 to 20 wt% relative to the weight of the polymer of Formula (I). In some embodiments, the cross-

linkable polymer composition of the present invention is the composition wherein the inorganic particle is present in an amount of from about 2 to 10 wt% relative to the weight of the polymer of Formula (I).

IV. METHODS OF PREPARING CROSS-LINKED POLYMERS

[0098] In some embodiments, the present invention provides a method of preparing a polymer, the method comprising: a) forming a reaction mixture comprising a cross-linkable polymer composition of the present invention, under conditions suitable to prepare the polymer.

[0099] The preparing of the polymer can be achieved by any suitable method, including, but not limited to, thermal or irradiative methods.

[0100] In some embodiments, the method of the present invention is the method further comprising heating the reaction mixture at a temperature of from about 70 °C to 140 °C.

[0101] In some embodiments, the method of the present invention is the method further comprising irradiating the reaction mixture at a wavelength less than 400 nm. In some embodiments, the method of the present invention is the method further comprising irradiating the reaction mixture at a wavelength of about 370 nm, at a lamp power of from 10 to 10,000 mW/cm^2; and for a time period of from 0.001 to 100 seconds. In some embodiments, the method of the present invention is the method wherein the irradiating provides a UV dose of from 10 to 10,000 mJ/cm^2. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a lamp power of about 100 mW/cm^2, or about 200 mW/cm^2, or about 500 mW/cm^2, or about 1,000 mW/cm^2, or about 2,500 mW/cm^2, or about 5,000 mW/cm^2, or about 7,500 mW/cm^2, or about 10,000 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a lamp power of about 100 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a lamp power of about 1,000 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a lamp power of about 10,000 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the irradiating is for a time period of from 0.001 to 10 seconds. In some embodiments, the method of the present invention is

the method wherein the irradiating is for a time period of from 5 to 10 seconds. In some embodiments, the method of the present invention is the method wherein the irradiating is for a time period of about 5 seconds. In some embodiments, the method of the present invention is the method wherein the irradiating is for a time period of about 10 seconds.

[0102] In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a wavelength of about 370 nm, at a lamp power of about 200 mW/cm^2; and for a time period of about 10 seconds. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a wavelength of about 370 nm, at a lamp power of about 100 mW/cm^2; and for a time period of about 10 seconds. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a wavelength of about 370 nm, at a lamp power of about 200 mW/cm^2; and for a time period of about 5 seconds. In some embodiments, the method of the present invention is the method wherein the irradiating is conducted at a wavelength of about 370 nm, at a lamp power of about 100 mW/cm^2; and for a time period of about 5 seconds.

[0103] In some embodiments, the method of the present invention is the method wherein the polymer of Formula (I) is PIM-DAA, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 12.5 mol% relative to PIM-DAA, the solvent is 1,3-dioxolane, and the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the polymer of Formula (I) is PIM-MAA, the crosslinker is trimethylolpropane tris(3-mercaptopropionate) and is present in an amount of about 25 mol% relative to PIM-DAA, the solvent is 1,3-dioxolane, and the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the polymer of Formula (I) is PIM-13/PIM-MAA (50/50) copolymer, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 25 mol% relative to PIM-13/PIM-MAA (50/50), the solvent is 1,3-dioxolane, and the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the polymer of Formula (I) is PIM-13/PIM-DAA (10/90) copolymer, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 50 mol% relative to PIM-13/PIM-DAA (10/90), the solvent is 1,3-dioxolane, the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) and is present in an amount of about 2.5 mol% relative to PIM-13/PIM-DAA (10/90), and the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the

method wherein the polymer of Formula (I) is PIM-13/PIM-DAA (20/80) copolymer, the crosslinker is 2,2'-(ethylenedioxy)diethanethiol and is present in an amount of about 50 mol% relative to PIM-13/PIM-DAA (20/80), the solvent is 1,3-dioxolane, and the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the polymer of Formula (I) is PIM-13/PIM-DAA (30/70) copolymer, the crosslinker is trimethylolpropane tris(3-mercaptopropionate) and is present in an amount of about 30 mol% relative to PIM-13/PIM-DAA (30/70), the solvent is 1,3-dioxolane, the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) and is present in an amount of about 5 mol% relative to PIM-13/PIM-DAA (30/70), and the irradiating is conducted at a lamp power of about 200 mW/cm^2. In some embodiments, the method of the present invention is the method wherein the polymer of Formula (I) is PIM-13/PIM-DAA (50/50) copolymer, the crosslinker is tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate and is present in an amount of about 25 mol% relative to PIM-13/PIM-DAA (50/50), the solvent is 1,3-dioxolane, the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) and is present in an amount of about 2.5 mol% relative to PIM-13/PIM-DAA (50/50), and the irradiating is conducted at a lamp power of about 200 mW/cm^2.

[0104] In some embodiments, the method of the present invention is the method wherein the method further comprising: curing the crosslinked polymer by sitting in the dark for 0 to 30 days, thereby preparing a cured crosslinked polymer.

[0105] In some embodiments, the method of the present invention is the method wherein the cured crosslinked polymer is substantially free of solvent.

[0106] In some embodiments, the method of the present invention is the method wherein the method further comprises prior to cross-linking: a2) coating a separator with the reaction mixture.

[0107] In some embodiments, the present invention provides a polymer prepared by the method of the present invention.

V. COATED SEPARATOR

[0108] In some embodiments, the present invention provides a separator coated with a polymer prepared by the method of the present invention.

[0109] In some embodiments, the present invention provides a coated separator comprising a porous membrane support; and a membrane layer on the porous membrane support comprising a polymer of the present invention.

[0110] FIG. 4A shows coated separator **100**, having porous support **110** having a first surface **111** and a second opposing surface **112**, and a polymer layer **130**.

[0111] The separator can include the polymer of the present invention alone or in combination with other components. In some embodiments, the present invention provides a coated separator, comprising:

a porous support having a first surface and a second opposing surface; and
a PIM polymer layer comprising a polymer of the present invention,
wherein the PIM polymer layer is coated on the first surface of the porous support.

[0112] The separator can include the polymer of the present invention alone or in combination with other components. In some embodiments, the present invention provides a multi-layer coated separator, comprising:

a porous support having a first surface and a second opposing surface;
a first polymer layer; and
a PIM polymer layer comprising a polymer of the present invention,
wherein the first polymer layer is coated on the first surface of the porous support, and the PIM polymer layer is coated on the first polymer layer.

[0113] FIG. 4B shows multi-layer coated separator **150**, having porous support **110** having a first surface **111** and a second opposing surface **112**, a first polymer layer **120**, and a polymer layer **130**.

[0114] In some embodiments, a ceramic coating layer **135** is present between the multi-layer coated separator **150** and the polymer layer **130**.

Porous support

[0115] In some embodiments, the pore size of porous support is between about 0.01 micrometers and 5 micrometers or more specifically between about 0.02 micrometers and 0.5 micrometers. The porosity of porous support may be between about 20% and 85%, or more specifically, between about 30% and 60%. One having ordinary skills in the art would understand that pore sizes may be effected by the composition of electrolyte that is provided in the pores of separator. For example, some components of separator (e.g., porous support

or first polymer layer) may swell when come in contact with some materials of electrolyte causing the pore size to change. Unless specifically noted, the pore size and other like parameter refer to components of separator before they come in contact with electrolyte.

[0116] Larger pore sizes allow using porous support that is much thicker than first polymer layer without significantly undermining the overall permeability of separator to first species. In some embodiments, the thickness of porous support is between about 5 micrometers and 500 micrometers, or in specific embodiment between about 5 micrometers and 50 micrometers, or more specifically between about 10 micrometers and 30 micrometers. In the same or other embodiments, the thickness of porous support may be between about 1 to 50 times greater than the thickness of first polymer layer or, more specifically, between about 5 and 25 times greater.

[0117] Some examples of suitable materials for porous support include, but are not limited, fluoro-polymeric fibers of poly(ethylene-co-tetrafluoroethylene (PETFE) and poly(ethylenechloro-co-trifluoroethylene) (e.g., a fabric woven from these used either by itself or laminated with a fluoropolymeric microporous film), polyvinylidene difluoride, polytetrafluoroethylene (PTFE), polystyrenes, polyarylether sulfones, polyvinyl chlorides, polypropylene, polyethylene (including LDPE, LLDPE, HDPE, and ultrahigh molecular weight polyethylene), polyamides, polyimides, polyacrylics, polyacetals, polycarbonates, polyesters, polyetherimides, polyimides, polyketones, polyphenylene ethers, polyphenylene sulfides, polymethylpentene, polysulfones non-woven glass, glass fiber materials, ceramics, metal oxides, composites of organic and inorganic species, and a polypropylene membrane. Porous support may also be supplied with an additional coating of a second suitable material including, but not limited to, PTFV, PVDF, and PETFE. These examples of porous support may or may not be commercially available under the designation CELGARD from Celanese Plastic Company, Inc. in Charlotte, N.C., USA, as well as Asahi Kasei Chemical Industry Co. in Tokyo, Japan, Tonen Corporation, in Tokyo, Japan, Ube Industries in Tokyo, Japan, Nitto Denko K.K. in Osaka, Japan. Nippon Kodoshi Corporation, in Kochi, Japan, Entek in Lebanon, Oregon, USA, SK Innovation in Jongro-Gu, Korea, Sumitomo Corporation, in Tokyo, Japan, Toray Industries in Tokyo, Japan, Dupont USA, in Wilmington, DE, USA, W-Scope in Japan, and Parker Hannifin Filtration Group, in Carson, CA, USA.

[0118] In some embodiments, the multi-layer coated separator is the separator wherein the porous support comprises polyethylene, polypropylene, poly(tetrafluoroethylene) (PTFE),

poly(vinyl chloride) (PVC), poly(vinylidene difluoride) (PVDF), cellulose, a ceramic, or combinations thereof. In some embodiments, the multi-layer coated separator is the separator wherein the porous support comprises polyethylene.

[0119] The porous support may have a thickness of between about 3 micrometers and 200 micrometers, or between about 5 micrometers and 100 micrometers, or between about 10 micrometers and 50 micrometers, or between about 9 micrometers and 25 micrometers, or between about 10 micrometers and 20 micrometers, or more specifically between about 15 micrometers and 30 micrometers. The porous support can have a thickness of about 5 micrometers, or about 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or about 20 micrometers.

First Polymer Layer

[0120] Selective blocking characteristics of one or more polymer layers used in a separator come from the composition or specific pore architectures of these layers. For purposes of this disclosure, the term "blocking" is referred to as sieving, selecting, or excluding. In some embodiments, the pore architectures of polymer layer manifest as networks of interconnected pores with small pore sizes, narrow pore-size distribution, high surface area, and high porosity as further described below. In some embodiments, the pore architectures of polymer layer manifest as an array of channels with small pore sizes, narrow pore-size distribution, high surface area, and high porosity as further described below. In addition to these blocking properties, the first polymer layer possesses various other properties making them suitable for electrochemical cell applications, such as chemical and electrochemical stability, wettability, thickness, thermal stability, and the like.

[0121] The blocking mechanism is based on chemical exclusion (non-wettable) or a size-exclusion effect transpired at a nanometer to sub-nanometer scale where tortuous, ionically percolating, pathways are established in polymer layers. For example, a polymer layer may allow Li-ions (or other like species described below) to pass while blocking larger electrolyte solvent or the like. The membrane may be formed from a ladder polymer with angular spiro centers and absence of rotatable bonds in the polymer backbone or bonds in the backbone with restricted bond rotation. These characteristics provide inefficient solid-state packing with porosity of between about 10% and 40% or, more specifically, between about 20% and 30% of the bulk powder. The pores may then be filled with an inorganic component, like aluminum oxide for example, leaving a non-porous or partially porous polymer layer.

[0122] The first polymer layer can include any suitable polymer. In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer is substantially insoluble in carbonate electrolytes. Representative carbonate electrolytes are described within. For example, the first polymer layer can be more than 50% insoluble in the carbonate electrolyte, or more than 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or more than 99% insoluble in the carbonate electrolyte.

[0123] The first polymer layer can include one or more different polymer layers. For example, the first polymer layer can include a first polymer layer, a second polymer layer, or more polymer layers. In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer comprises polyacrylonitrile, poly(acrylonitrile-methyl acrylate), poly(acrylonitrile-co-methacrylic acid), poly(acrylonitrile-acrylic acid), poly(acrylonitrile-itaconic acid), poly(acrylonitrile-methyl methacrylate), poly(acrylonitrile-itaconic acid-methyl acrylate), poly(acrylonitrile-methacrylic acid-methyl acrylate), poly(acrylonitrile-vinyl pyridine), poly(acrylonitrile-vinyl chloride), poly(acrylonitrile-vinyl acetate), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), a second polymer of intrinsic microporosity different from the first polymer of intrinsic microporosity, or combinations thereof. In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer comprises poly(acrylonitrile-co-methyl acrylate), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), the second polymer of intrinsic microporosity different from the first polymer of intrinsic microporosity, or combinations thereof.

PIM Polymer Layer

[0124] The PIM polymer layer useful in the coated separator of the present invention can include a polymer prepared by the methods of the present invention using the cross-linkable polymer composition of the present invention.

[0125] Other polymers of intrinsic microporosity useful in the electrochemical device of the present invention include those described in U.S. Patent Nos. 10,710,065, and 11,394,082, U.S. Publication No. 2021/0309802, and 2019/0326578, each of which is incorporated herein by reference in its entirety. In some embodiments, the PIM polymer layer is a polymer of the present invention.

[0126] To achieve very high ion transport required to enable fast charge and high power applications, high free volume and microporosity are sought after. Polymers presenting these

properties are so-called high free volume polymers. These highly permeable polymers have been applied mostly to gas separations. Some examples include certain substituted polyacetylenes (e.g. PTMSP), some perfluoropolymers (e.g. Teflon AF), certain poly(norbornene)s, polymers of intrinsic microporosity, and some polyimides. Their microporosity has been demonstrated by molecular modelling and positron lifetime spectroscopy (PALS). Highly permeable polyacetylenes have bulky side groups that inhibit conformational change and force the backbone into a twisted shape. These rigid polymer macromolecules cannot pack properly in the solid state, resulting in high free volume. The free volume distribution comprises disconnected elements as in glassy polymers and continuous microvoids. In Teflon perfluoropolymers their high free volume is due to a high barrier to rotation between neighbouring dioxolane rings, coupled with weak interchain interactions, which are well known for fluoropolymers, leading to low packing density and hence high permeability. In the case of poly(norborene)s and PTMSP, the presence of bulky trimethylsilyl groups on the ring greatly restricts the freedom of the polymer to undergo conformational change. In polymers of intrinsic microporosity (PIMs), molecular linkers containing points of contortion are held in non-coplanar orientation by rigid molecules, which do not allow the resulting polymers to pack closely and ensure high microporosity. The PIMs concept has been reported for polymides [P M Budd and N B McKewon, "Highly permeable polymers for gas separation membranes, Polymer Chemistry, 1, 63-68, 2010].

[0127] There are two different types of PIMs, i) non-network (linear) polymers which may be soluble in organic solvents, and ii) network polymers which are generally insoluble, depending on the monomer choice. PIMs possess internal molecular free volume (IMFV), which is a measure of concavity and is defined by Swager as the difference in volume of the concave unit as compared to the non-concave shape [T M Long and T M Swager, "Minimization of Free Volume: Alignment of Triptycenes in Liquid Crystals and Stretched Polymers", Adv. Mater, 13, 8, 601-604, 2001]. While the intrinsic microporosity in linear PIMs is claimed to derive from the impenetrable concavities given by their contorted structures, in network PIMs, microporosity is also claimed to derive from the concavities associated with macrocycles. In non-network PIMs, rotation of single bonds has to be avoided, whereas the branching and crosslinking in network PIMs is thought to avoid structural rearrangement that may result in the loss of microporosity (McKeown, 2010), so that single bonds can be present without loss of microporosity. In general, it has been observed that network PIMs possess greater microporosity than non-network PIMs due to

their macrocyclization [N B McKewon, P M Budd, "Exploitation of Intrinsic Microporosity in Polymer-Based materials", Macromolecules, 43, 5163-5176, 2010]. However, since prior art network PIMs are not soluble, they can only be incorporated into a membrane if mixed as fillers with microporous soluble materials, which include soluble PIMs or other soluble polymers. There is a strict requirement in non-network PIMs that there are no single bonds in the polymer backbone, to prevent rotational freedom and so provide intrinsic microporosity. Highly rigid and contorted molecular structures are required, providing awkward macromolecular shapes that cannot pack efficiently in space. Molecules with awkward shapes are those that pose packing problems due to their concavities. However, in order to have microporosity in non-network PIMs, concave shape molecules are not sufficient as the voids must be sufficiently interconnected for transport to occur with minimal energy (i.e. intrinsic microporosity) [N B McKewon, P M Budd, "Exploitation of Intrinsic Microporosity in Polymer-Based materials", Macromolecules, 43, 5163-5176, 2010]. Non-network PIMs may be soluble, and so suitable for casting a membrane by phase inversion, or for use coating a support membrane to make a thin film composite. However, their solubility in a range of solvents restricts their applications in organic solvent nanofiltration [Ulbricht M, Advanced functional polymer membranes. Single Chain Polymers, 47, 2217-2262, 2006].

[0128] U.S. Pat. No. 7,690,514 B2 describes materials of intrinsic microporosity comprising organic macromolecules comprised of a first generally planar species connected by linkers having a point of contortion such that two adjacent first planar species connected by a linker are held in non-coplanar orientation. Preferred points of contortion are spiro groups, bridged ring moieties and sterically congested bonds around which there is restricted rotation. These non-network PIMs may be soluble in common organic solvents, allowing them to be cast into membranes, or coated onto other support membranes to make a thin film composite.

[0129] PIM-1 (soluble PIM) membranes exhibit gas permeabilities which are exceeded only by very high free volume polymers such as Teflon AF2400 and PTMSP, presenting selectivities above Robeson's 1991 upper bound for gas pairs such as CO_2/CH_4 and O_2/N_2. Studies have shown that permeability is enhanced by methanol treatment, helping flush out residual casting solvent and allowing relaxation of the chains [P M Budd and N B McKewon, D Fritsch, "Polymers of Intrinsic Microporosity (PIMs): High free volume polymers for membrane applications", Macromol Symp, 245-246, 403-405, 2006].

[0130] A range of polyimides with characteristics similar to a microporous polymer (PIM) were prepared by Ghanem et al. and membrane gas permeation experiments showed these PIM-Polyimides to be among the most permeable of all polyimides and to have selectivities close to the upper bound for several important gas pairs [B G Ghanem, N B McKeown, P M Budd, N M Al-Harbi, D Fritsch, K Heinrich, L Starannikova, A Tokarev and Y Yampolskii, "Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic micro porosity: PIM-polyimides", Macromolecules, 42, 7781-7888, 2009].

[0131] U.S. Pat. No. 7,410,525 B1, describes polymer/polymer mixed matrix membranes incorporating soluble polymers of intrinsic microporosity as microporous fillers for use in gas separation applications.

[0132] International Patent Publication No. WO 2005/113121 (PCT/GB2005/002028) describes the formation of thin film composite membranes from PIMs by coating a solution of PIMs in organic solvent onto a support membrane, and then optionally crosslinking this PIM film to enhance its stability in organic solvents.

[0133] In order to improve the stability of soluble-PIMs membranes U.S. Pat. No. 7,758,751 B1, describes high performance UV-crosslinked membranes from polymers of intrinsic microporosity (PIMs) and their use in both gas separations, and liquid separations involving organic solvents such as olefin/paraffin, deep desulfurization of gasoline and diesel fuels, and ethanol/water separations.

[0134] In some embodiments, a PIM polymer layer comprises a polymer having a chain comprised of repeating units bonded to each other. Each unit may include a first generally planar species comprising at least one aromatic ring and also comprising a rigid linker having a site of contortion, which is a spiro group, a bridged ring moiety, or a sterically congested single covalent bond. The rigid linker restricts rotation of the first planar species in a non-coplanar orientation. In some embodiments, at least 50% by mole (or 70%, 80%, or even 90%) of the first planar species in the chain are connected by the rigid linkers to a maximum of two other planar species and being such that it does not have a cross-linked, covalently bonded 3-dimensional structure. As such, this polymer may include rigid linkers having a site of contortion. Since these polymer chains do not pack together by virtue of their rigid contorted structure, the polymer layer possesses intrinsic microporosity and, in some cases, nanoporosity. As such, this combination of non-packed and non-crosslinked polymer chains

extends in three dimensions. It may be also considered as a non-network polymer. Cross-linked polymers are also within the scope.

[0135] In some embodiments, the surface area of the PIM polymer layer (as measured by nitrogen adsorption or a related technique of the dry powder prior to membrane processing) prior to infilling with an inorganic component may be at least 200 m^2/g or at least 500 m^2/g such as between 200 m^2/g and 2200 m^2/g or more specifically between 600 m^2/g and 900 m^2/g. Representative methods for measuring surface area include nitrogen adsorption BET. The surface area is directly related to the porosity, essential for efficient transport of supporting electrolyte between electrodes and higher power cell operation. Typical porosities range from 20% to 70% or more specifically 30% to 60%. The surface area of the PIM polymer layer can be from 100 m^2/g to 3000 m^2/g, such as 100 m^2/g, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400, 2500, 2600, 2700, 2800, 2900, or 3000 m^2/g. In some embodiments, the multi-layer coated separator is the separator wherein the polymer layer has a surface area of from 100 m^2/g to 3000 m^2/g, as measured by nitrogen adsorption BET.

[0136] In some embodiments, the multi-layer coated separator is the separator wherein the average pore diameter of the polymer layer prior to infilling with an inorganic component is of less than 100 nm, or from about 0.1 nm to about 20 nm, or from about 0.1 nm to about 10 nm, or from about 0.1 nm to about 5 nm, or from about 0.1 nm to about 2 nm, or from about 0.1 nm to about 1 nm. For example, the average pore diameter of the polymer layer can be less than about 10 nm, or less than about 9, 8, 7, 6, 5, 4, 3, 2, or 1 nm. For example, the average pore diameter of the polymer layer can be about 10 nm, or about 9, 8, 7, 6, 5, 4, 3, 2, or 1 nm. This pore diameter ensures that some materials (e.g., materials that have unit sizes greater than the pore diameter) are blocked by the polymer layer, while other materials are allowed to pass (e.g., materials with smaller unit sizes). In some embodiments, the multi-layer coated separator is the separator wherein the polymer layer has an average pore diameter of from 0.1 nm to 10 nm. In some embodiments, the multi-layer coated separator is the separator wherein the polymer layer has an average pore diameter of from 0.1 nm to 2 nm. In some embodiments, the multi-layer coated separator is the separator wherein the polymer layer has an average pore diameter of from 0.1 nm to 1 nm.

[0137] In some embodiments, the multi-layer coated separator is the separator wherein the number average molecular weight (M_n) of the polymer layer is between $1x10^3$ and $2000x10^3$

kg/mol or, more specifically, between $15x10^3$ and $500x10^3$ kg/mol or between $20x10^3$ and $200x10^3$ kg/mol. Larger number average molecular weight polymers contribute to enhanced mechanical properties of the formed membrane.

[0138] The PIM polymer layer can be a film cast, sprayed or coated from solution (e.g., onto the porous support), a composite comprised of a plurality of individual membrane layers, a free-standing film, or a supported film (e.g., by a porous support).

[0139] In some embodiments, the multi-layer coated separator is the separator wherein the polymer layer has a thickness of between about 5 nanometers and 20 micrometers, or between about 100 nanometers and 10 micrometers, or more specifically between about 500 nanometers and 5 micrometers.

[0140] The microporosity of a polymer layer is demonstrated by its high surface area (approximately 680 – 850 m^2/g) determined using nitrogen adsorption measurements (BET calculation). The presence of the cyano and methyl groups is optional, they may be omitted or replaced with other simple substituents. Each phenyl group may contain one or more substituents. Additionally, the nature and arrangement of substituents on the spiro-indane moiety may be chosen to provide any desirable configuration around the carbon atom common to both 5-membered rings.

VI. ELECTROLYTE

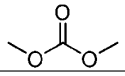
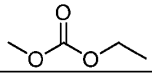
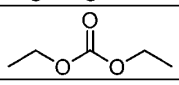
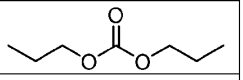
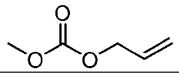
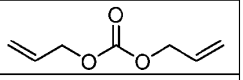
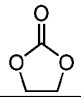
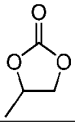
[0141] The electrochemical cell of the present invention also includes an electrolyte, such as a carbonate-based electrolyte. The electrolyte can have a variety of components, such as an alkyl carbonate, a fluorinated carbonate, a diisocyanate, a lithium salt, or combinations thereof. The present invention also includes an electrolyte having an alkyl carbonate, a fluorinated carbonate, a diisocyanate, and a lithium salt.

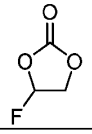
[0142] In some embodiments, the present invention provides an electrolyte comprising an alkyl carbonate, a fluorinated carbonate, a diisocyanate, and a first lithium salt. In some embodiments, the electrolyte comprises a second lithium salt different from the first lithium salt.

[0143] In some embodiments, the electrolyte comprises a carbonate electrolyte. A carbonate electrolyte can have the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{1-6} haloalkyl, C_{3-6} cycloalkyl, or C_{6-12} aryl, wherein

each aryl can be substituted with 1, 2, 3, 4, or 5 halogens, alternatively R' and R" can be combined to form a 5 to 6 membered heterocycloalkyl that can be substituted with 0, 1, 2, 3, 4, or 5 halogens. In some embodiments, the carbonate electrolyte can have the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-6} alkyl, C_{2-6} alkenyl, or C_{1-6} haloalkyl, alternatively R' and R" can be combined to form a 5 membered heterocycloalkyl that can be substituted with 0, 1, or 2 halogens. In some embodiments, the carbonate electrolyte can have the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-3} alkyl, or C_{1-4} haloalkyl, alternatively R' and R" can be combined to form a 5 membered heterocycloalkyl that can be substituted with 0, 1, or 2 halogens. The carbonate electrolyte can be an alkyl carbonate of the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-6} alkyl. The carbonate electrolyte can be a fluorinated carbonate of the formula R'-OC(O)O-R", where R' is C_{1-6} alkyl, or C_{1-6} haloalkyl, and R" is C_{1-6} haloalkyl, wherein each haloalkyl is a fluoroalkyl, alternatively R' and R" can be combined to form a 5 to 6 membered heterocycloalkyl that can be substituted with 0, 1, 2, 3, 4, or 5 fluorine.

[0144] Representative alkyl carbonates of the electrolyte include, but are not limited to:

Dimethyl carbonate	
Ethyl methyl carbonate	
Diethyl carbonate	
Dipropyl carbonate	
Allyl methyl carbonate	
Diallyl carbonate	
Ethylene carbonate	
Vinylene carbonate	
Propylene carbonate	

Fluoroethylene carbonate	

[0145] In some embodiments, the alkyl carbonate is dimethyl carbonate.

[0146] Representative fluorinated carbonates of the electrolyte include, but are not limited to, fluoroethylene carbonate, $CH_3OC(O)OCH_2CF_3$, $CH_3OC(O)OCH_2CF_2CHF_2$, $CH_3OC(O)OCH_2CF_2CHF_2$, $CF_3CH_2OC(O)OCH_2CF_3$, $CH_3OC(O)OCH_2CF_2CF_2CF_3$, $CH_3CH_2OC(O)OCH_2CF_2CF_3$, $CH_3CH_2OC(O)OCH_2CF_2CHF_2$, or $CH_3OC(O)OCH_2CF_2CF_2CF_3$.

[0147] Representative diisocyanates of the electrolyte include, but are not limited to, tolylene-2,4-diisocyanate, or tolylene-2,6-diisocyanate.

[0148] The lithium salt of the electrolyte compositions of the present invention can be any suitable lithium salt. For example, suitable lithium salts include, but are not limited to, lithium bis(fluorosulfonyl)imide, lithium hexafluorophosphate, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, lithium bis(trifluoromethanesulfonyl)imide, lithium difluorophosphate, lithium nitrate, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, or combinations thereof. In some embodiments, the lithium salt can be lithium bis(fluorosulfonyl)imide, lithium hexafluorophosphate, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, lithium bis(trifluoromethanesulfonyl)imide, lithium difluorophosphate, lithium nitrate, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, or combinations thereof.

[0149] In some embodiments, the electrolyte composition is the electrolyte composition wherein the first lithium salt includes lithium bis(fluorosulfonyl)imide (LiFSi), lithium hexafluorophosphate, or combinations thereof. In some embodiments, the electrolyte composition is the electrolyte composition wherein the first lithium salt includes lithium bis(fluorosulfonyl)imide (LiFSi).

[0150] The first lithium salt can be present in the electrolyte composition in any suitable amount. For example, the first lithium salt can be present in the electrolyte composition in an amount of from 0.1 to 20 mol%, from 0.1 to 20 mol%, from 1 to 20 mol%, from 5 to 20 mol%, from 5 to 15 mol%, from 8 to 12 mol%, or from 9 to 11 mol%. Representative

amounts of the first lithium salt in the electrolyte compositions of the present invention include, but are not limited to, about 5 mol%, or about 6, 7, 8, 9, 10, 11, 12, 13, 14, or about 15 mol%.

[0151] The electrolyte composition of the present invention can include one or more lithium salts. For example, the electrolyte composition can include 1, 2, 3, 4, or more different lithium salts as defined above. In some embodiments, the electrolyte composition is the electrolyte composition comprising a single lithium salt. In some embodiments, the electrolyte composition is the electrolyte composition comprising two different lithium salts. In some embodiments, the electrolyte composition is the electrolyte composition comprising three different lithium salts.

[0152] The electrolyte compositions of the present invention can also include a second lithium salt that is different from the first lithium salt. In some embodiments, the electrolyte composition is the electrolyte composition including a second lithium salt that is different from the first lithium salt.

[0153] In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, lithium bis(trifluoromethanesulfonyl)imide, lithium difluorophosphate, lithium nitrate, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, or combinations thereof. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, or combinations thereof. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium difluoro(oxalato)borate. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium nitrate.

[0154] The second lithium salt can be present in the electrolyte composition in any suitable amount. For example, the second lithium salt can be present in the electrolyte composition in an amount of from 0.1 to 10 mol%, from 0.1 to 5 mol%, from 0.5 to 5 mol%, from 0.5 to 4 mol%, from 0.5 to 3.5 mol%, from 1 to 3 mol%, from 1.0 to 2.5 mol%, or from 1.5 to 2.5

mol%. Representative amounts of the second lithium salt in the electrolyte compositions of the present invention include, but are not limited to, about 1.5 mol%, or about 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, or about 2.5 mol%.

[0155] In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of from 0.1 to 5 mol%. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of from 0.5 to 3.5 mol%. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of 1 to 3 mol%. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of from 1.5 to 2.5 mol%.

[0156] In some embodiments, the present invention provides an electrolyte comprising:

ethyl methyl carbonate in an amount from 25% to 75% (mol/mol);
ethylene carbonate in an amount from 25% to 75% (mol/mol);
lithium hexafluorophosphate in an amount from 0.1% to 20% (mol/mol);
vinylene carbonate in an amount from 0% to 10% (mol/mol); and
fluoroethylene carbonate in an amount from 0% to 10% (mol/mol).

[0157] In some embodiments, the present invention provides an electrolyte comprising:

dimethyl carbonate in an amount of from 25% to 75% (mol/mol);
fluoroethylene carbonate in an amount of from 20% to 65% (mol/mol);
tolylene-2,6-diisocyanate in an amount of from 0.1% to 10% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of from 1% to 20% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of from 0.1% to 10% (mol/mol).

[0158] In some embodiments, the present invention provides an electrolyte comprising:

dimethyl carbonate in an amount of about 48% (mol/mol);
fluoroethylene carbonate in an amount of about 39% (mol/mol);
tolylene-2,6-diisocyanate in an amount of about 1% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of about 10% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of about 2% (mol/mol).

VII. ELECTROCHEMICAL CELL

[0159] In another embodiment, the present invention provides an electrochemical cell comprising an anode; a cathode; a separator between the anode and cathode, wherein the separator is coated on one side with a polymer prepared by the method of the present invention; and an electrolyte composition.

[0160] In some embodiments, the electrochemical device is an electrochemical cell. In some embodiments, an electrochemical cell includes a positive electrode, a negative electrode, a separator, and an electrolyte.

[0161] In some embodiments, the present invention provides an electrochemical cell comprising: an anode; a cathode; a coated separator of the present invention; and an electrolyte. FIG. 5A shows the electrochemical cell **200**, having anode **210**, cathode **220**, and the coated separator **100**. The separator **100** is disposed between the anode **210** and the cathode **220**. The separator provides electronic isolation between the anode and the cathode. At least a portion of the electrolyte is disposed within the separator.

[0162] In some embodiments, the present invention provides an electrochemical cell comprising: an anode; a cathode; a multi-layer coated separator of the present invention; and an electrolyte. FIG. 5B shows the electrochemical cell **200**, having anode **210**, cathode **220**, and the multi-layer coated separator **150**. The separator **100** is disposed between the anode **210** and the cathode **220**. The separator provides electronic isolation between the anode and the cathode. At least a portion of the electrolyte is disposed within the separator.

[0163] In some embodiments, the electrochemical cell is the electrochemical cell wherein the multi-layer coated separator is between the anode and the cathode. In some embodiments, the electrochemical cell is the electrochemical cell wherein the multi-layer coated separator is oriented such that the first surface of the support material is oriented towards the anode.

[0164] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte is an electrolyte of the present invention. In some embodiments, the electrolyte can be a carbonate electrolyte.

[0165] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises:

ethyl methyl carbonate in an amount from 25% to 75% (mol/mol);
ethylene carbonate in an amount from 25% to 75% (mol/mol);
lithium hexafluorophosphate in an amount from 0.1% to 20% (mol/mol);
vinylene carbonate in an amount from 0% to 10% (mol/mol); and
fluoroethylene carbonate in an amount from 0% to 10% (mol/mol)

[0166] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises:

dimethyl carbonate in an amount of from 25% to 75% (mol/mol);
fluoroethylene carbonate in an amount of from 20% to 65% (mol/mol);
tolylene-2,6-diisocyanate in an amount of from 0.1% to 10% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of from 1% to 20% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of from 0.1% to 10% (mol/mol).

[0167] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises:

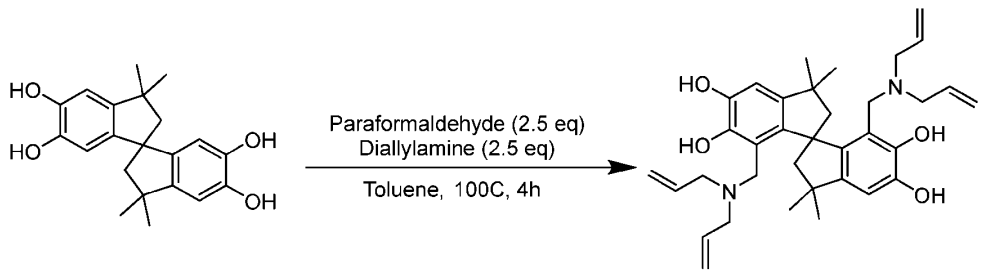
dimethyl carbonate in an amount of about 48% (mol/mol);
fluoroethylene carbonate in an amount of about 39% (mol/mol);
tolylene-2,6-diisocyanate in an amount of about 1% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of about 10% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of about 2% (mol/mol).

[0168] In some embodiments, the electrochemical device is a lithium-ion battery with a carbon-based, metallic, or metalloid anode and a metal oxide or conversion cathode.

VIII. EXAMPLES

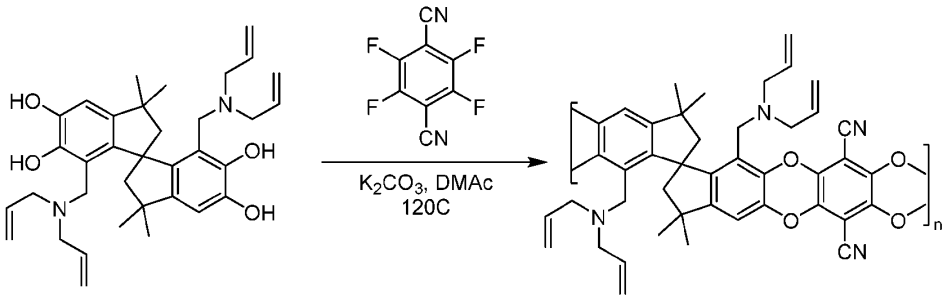
A. Preparation of Polymers

Preparation of SBI-DAA (1):



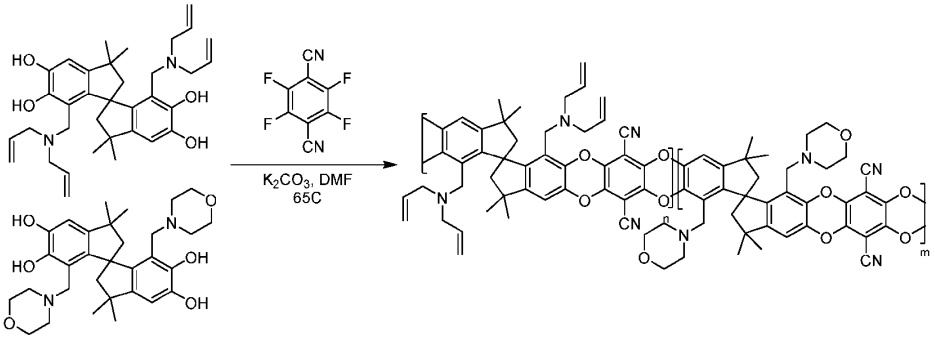
[0169] To a 2L, two neck round bottom flask equipped with a vacuum adapter and septum was added paraformaldehyde (14.7 g, 490 mmol, 2.5 eq), diallylamine (47.6 g, 490 mmol, 2.5 eq), and toluene (1L). This mixture was then heated to 100°C under nitrogen for 1 hour and full dissolution of reagents before 3,3,3′,3′-Tetramethyl-1,1′-spirobiindane-5,5′,6,6′-tetraol (66.7 g, 196 mmol, 1 eq) was added and the reaction mixture further stirred under nitrogen at that temperature for 4 hours. The reaction mixture was then cooled to room temperature and solvent removed by rotary evaporation. The resulting oily mixture was triturated with isopropanol, and filtered, resulting in a white powder that was further purified by recrystallization in isopropanol to yield SBI-DAA (59.8 g, 54.6 % yield) as a white to off-white solid. ^{1}H NMR (400 MHz, DMSO-d6, δ): 11.51 (2H, s), 8.26 (2H, s), 6.51 (2H, s), 5.63 (4H, m), 5.12 (4H, dd), 3.34 (4H, s), 2.88 (8H, m), 2.14 (4H, dd), 1.30 (6H, s), 1.19 (6H, s).

Preparation of PIM-DAA (2):



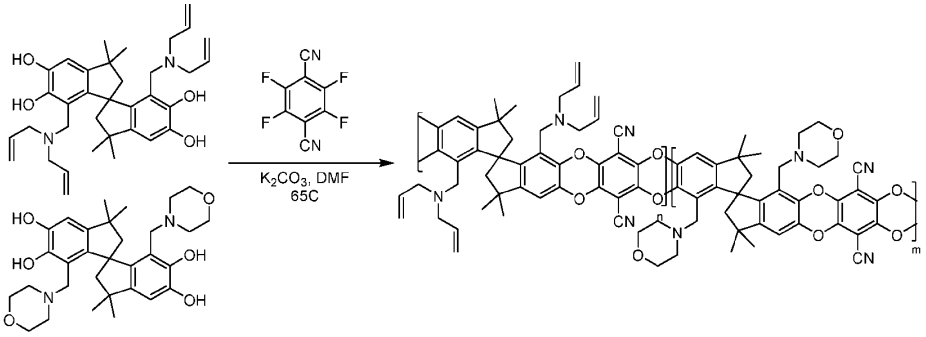
[0170] To a 2L, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (12 g, 60 mmol, 1 eq), SBI-diallylamine (**1**, 34.2 g, 61.2 mmol, 1.02 eq.), and anhydrous DMF (640 mL). The reaction mixture was then heated to 65°C and anhydrous potassium carbonate (33.84 g, 244.8, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65°C for 24 hours, after which it was precipitated into water (2L), vacuum filtered, washed with additional water (750 mL) and ethanol (750 mL), and dried *in-vacuuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-DAA (30.79 g, 76%, M_w = 139 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.84 (1H, s), 5.52 (2H, s), 5.00 (4H, m), 3.40 – 2.20 (6H, m), 1.38 (3H, s), 1.33 (3H, s).

Preparation of PIM-13/DAA (10/90) (3)



[0171] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-diallylamine (**1**, 7.694 g, 13.77 mmol, 0.918 eq.), SBI-morpholine (0.824 g, 1.53 mmol, 0.102 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 120 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65 °C for 24 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (10/90) (8.26 g, 81%, M_w = 63.2 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (reference 2H, s), 5.50 (3.64H, s), 4.98 (7.18H, d), 3.40-2.20 (16.22H, m), 1.38 (5.80H, s), 1.34 (6.00H, s).

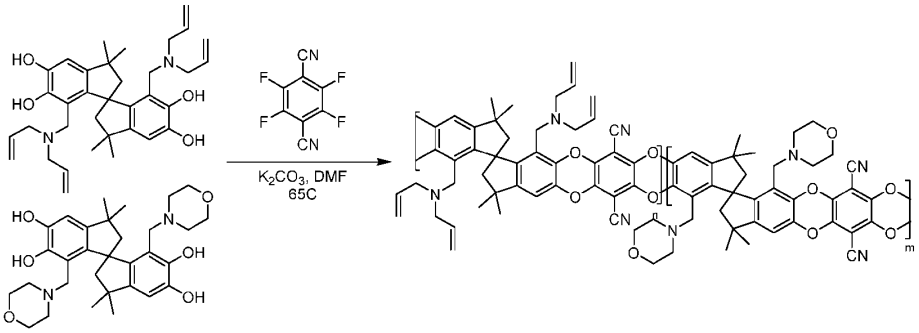
Preparation of PIM-13/DAA (20/80) (4)



[0172] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-diallylamine (**1**,

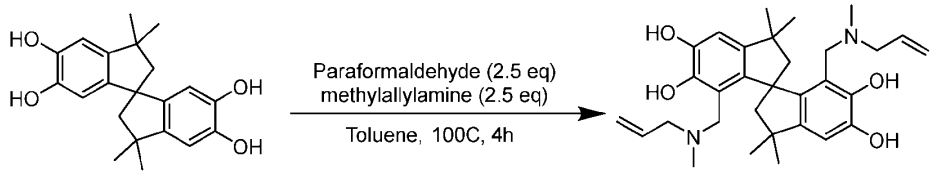
6.839 g, 12.24 mmol, 0.816 eq.), SBI-morpholine (1.648 g, 3.06 mmol, 0.204 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 65 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65 °C for 24 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (20/80) (8.07 g, 80%, M_w = 112.8 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (reference 2H, s), 5.52 (3.16H, s), 4.98 (6.18H, d), 3.60-2.20 (16.88H, m), 1.38 (5.34H, s), 1.34 (6.00H, s).

Preparation of PIM-13/DAA (30/70) (5)



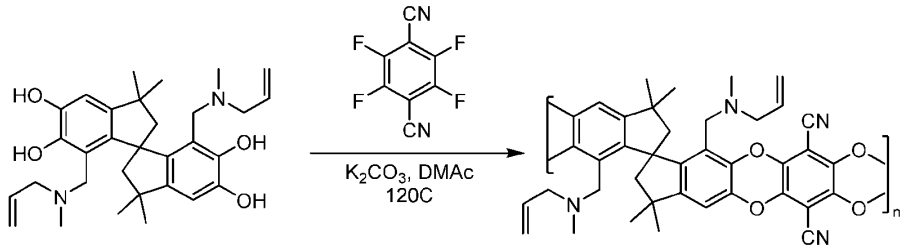
[0173] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-diallylamine (**1**, 5.984 g, 10.71 mmol, 0.714 eq.), SBI-morpholine (2.473 g, 4.59 mmol, 0.306 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 65 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65 °C for 24 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (30/70) (8.18 g, 81%, M_w = 56.6 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.83 (reference 2H, s), 5.51 (2.66H, s), 4.98 (5.19H, d), 3.60-2.20 (18.67H, m), 1.38 (5.24H, s), 1.34 (6.00H, s).

Preparation of SBI-MAA (6):



[0174] To a 2L, two neck round bottom flask equipped with a vacuum adapter and septum was added paraformaldehyde (11.02 g, 367 mmol, 2.5 eq), N-methylallylamine (26.12 g, 367 mmol, 2.5 eq), and toluene (1L). This mixture was then heated to 100°C under nitrogen for 1 hour and full dissolution of reagents before 3,3,3′,3′-Tetramethyl-1,1′-spirobiindane-5,5′,6,6′-tetraol (50 g, 147 mmol, 1 eq) was added and the reaction mixture further stirred under nitrogen at that temperature for 4 hours. The reaction mixture was then cooled to room temperature and solvent removed by rotary evaporation. The resulting oily mixture was triturated with isopropanol, and filtered, resulting in a white powder that was further purified by recrystallization in isopropanol to yield SBI-MAA (41.1 g, 55.2 % yield) as a white to off-white solid. ^{1}H NMR (400 MHz, DMSO-d6, δ): 11.51 (2H, bs), 8.26 (2H, bs), 6.51 (2H, s), 5.65 (4H, m), 5.12 (4H, dd), 3.08 (4H, m), 2.89 (4H, m), 2.11 (4H, dd), 1.99 (3H, s), 1.30 (6H, s), 1.19 (6H, s).

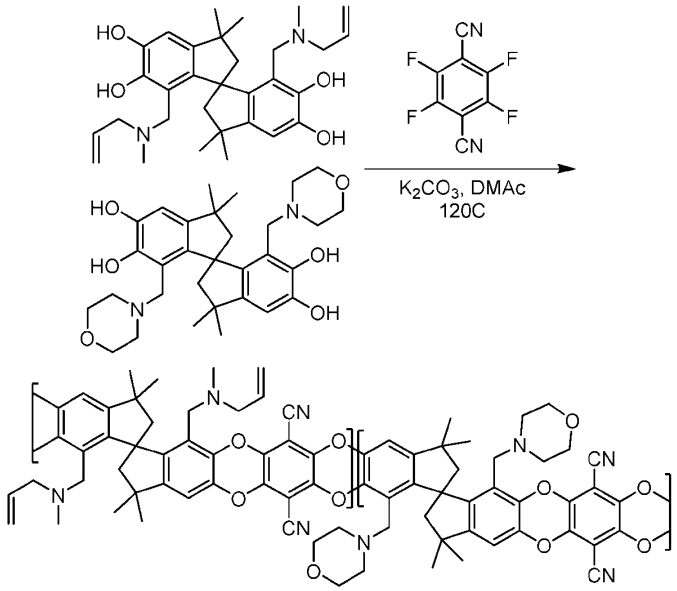
Preparation of PIM-MAA (7):



[0175] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-methylallylamine (**6**, 7.45 g, 14.7 mmol, 0.98 eq.), and anhydrous DMAc (135 mL). The reaction mixture was then heated to 120 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 120°C for 2 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a

concentration of 25 mg/mL for 24 hours and filtering to yield PIM-MAA (7.02 g, 76%, M_w = 214 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (2H, s), 5.61 (2H, s), 5.01 (4H, d), 3.40 – 2.60 (10H, m), 2.17 (2H, s), 1.86 (6H, s), 1.36 (6H, s), 1.32 (6H, s).

Preparation of PIM-13/MAA (50/50) (8):



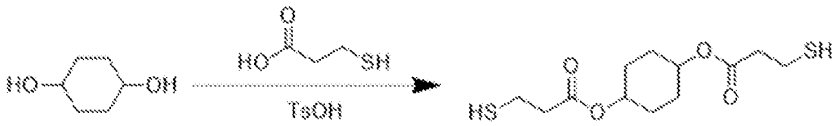
[0176] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-methylallylamine (**6**, 3.724 g, 7.35 mmol, 0.49 eq.), SBI-morpholine (3.959 g, 7.35 mmol, 0.49 eq) and anhydrous DMAc (135 mL). The reaction mixture was then heated to 120 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 120°C for 2 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/MAA (50/50) (8.86 g, 94%, M_w = 95.0 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.79 (1H, s), 5.59 (0.5H, s), 5.00 (1H, d), 2.99 (9H, m), 1.85 (1.5H, s), 1.34 (6H, d).

B. Preparation of Crosslinkers

Table 1: Poly-Thiol Crosslinkers

Crosslinker	Name	CAS
Dithiol	2,2'-(Ethylenedioxy)diethanethiol	14970-87-7
Trithiol	Trimethylolpropane tris(3-mercaptopropionate)	33007-83-9
Tetrathiol	Pentaerythritol tetrakis(3-mercaptopropionate)	7575-23-7
Hexathiol	Dipentaerithritol hexakis(3-mercaptopropionate)	25359-71-1
CD-BMP	Cyclohexane-1,4-diyl bis(3-mercaptopropanoate)	20249-12-1
2EG-BMP	Di(ethylene glycol) bis(3-mercaptopropionate)	22504-50-3
3EG-BMP	Tri(ethylene glycol) bis(3-mercaptopropionate)	
4EG-BMP	Tetra(ethylene glycol) bis(3-mercaptopropionate)	68891-92-9
6EG-BMP	Hexa(ethylene glycol) dithiol	89141-22-0
TMP-EI	Tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate	36196-44-8

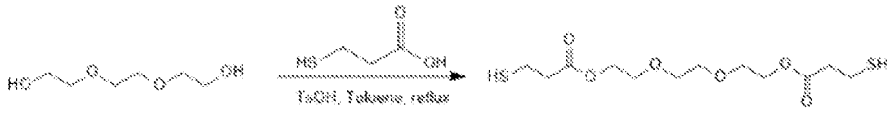
Preparation of cyclohexane-1,4-diyl bis(3-mercaptopropanoate) (9):



[0177] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added 1,4-cyclohexanediol (10 g, 86.09 mmol, 1 eq.), 3-mercaptopropionic acid (19.2 g, 180.80 mmol, 2.1 eq.), tosylic acid monohydrate (0.82 g, 4.30 mmol, 0.05 eq.), and toluene (125 mL). The reaction mixture was then heated to reflux. The reaction mixture was stirred under nitrogen at reflux for 18 hours, after which the reaction mixture was extracted with ethyl acetate (400 mL), in a separatory funnel. The ethyl acetate layer was separated

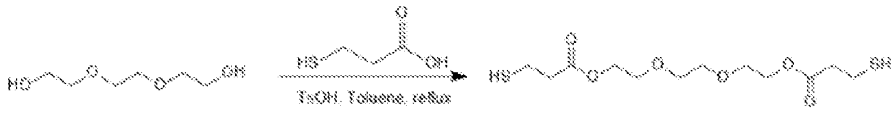
from the toluene mixture and dried over excess magnesium sulfate. The crude product mixture was purified using a silica column was set up for purification using a gradient of 0 to 50% ethyl acetate in hexanes to yield pure cyclohexane-1,4-diyl bis(3-mercaptopropanoate) (9.72 g, 34%) as a white to off-white solid. 1H NMR (400 MHz, CDCl3, δ): δ 4.86 (2H, m), 2.76 (4H, m), 2.63 (4H, m), 1.96 (2H, m), 1.81 (2H, m), 1.71 (2H, m), 1.55 (2H, m).

Preparation of Tri(ethylene glycol) bis(3-mercaptopropionate) (10):



[0178] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added triethylene glycol (15.00 g, 99.9 mmol, 1 eq.), 3-mercaptopropionic acid (22.26 g, 210.00 mmol, 2.1 eq.), tosylic acid monohydrate (0.95 g, 4.99 mmol, 0.05 eq.), and toluene (100 mL). The reaction mixture was then heated to reflux. The reaction mixture was stirred under nitrogen at reflux for 18 hours, after which the reaction mixture was extracted with ethyl acetate (400 mL), in a separatory funnel. The ethyl acetate layer was separated from the toluene mixture and washed three times with 200 mL of deionized water, one time with 200 mL of brine. The ethyl acetate layer was then dried over excess magnesium sulfate. The washed product was dried overnight, in a vacuum oven at 55 °C to yield pure tri(ethylene glycol) bis(3-mercaptopropionate) (19.78 g, 60.7%). 1H NMR (400 MHz, CDCl3, δ): δ 4.23 (4H, t), 3.67 (4H, t), 2.74 (4H, t), 2.65 (4H, t), 1.65 (2H, t).

Preparation of Tetra(ethylene glycol) bis(3-mercaptopropionate) (11):



[0179] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetraethylene glycol (15.00 g, 77.23 mmol, 1 eq.), 3-mercaptopropionic acid (17.21 g, 162.00 mmol, 2.1 eq.), tosylic acid monohydrate (0.73 g, 3.86 mmol, 0.05 eq.), and toluene (100 mL). The reaction mixture was then heated to reflux. The reaction mixture was stirred under nitrogen at reflux for 18 hours, after which the reaction mixture was extracted with ethyl acetate (400 mL), in a separatory funnel. The ethyl acetate layer was separated from the toluene mixture and washed three times with 200 mL of deionized water,

one time with 200 mL of brine. The ethyl acetate layer was then dried over excess magnesium sulfate. The washed product was dried overnight, in a vacuum oven at 55 °C to yield pure tetra(ethylene glycol) bis(3-mercaptopropionate) (15.81 g, 55.3%). 1H NMR (400 MHz, CDCl3, δ): δ 4.23 (4H, t), 3.67 (4H, t), 3.62 (8H, s), 2.73 (4H, t), 2.65 (4H, t), 1.65 (2H, t).

A. Preparation of Crosslinked PIMs

Example 1: Assessment for photobleaching or UV-initiated crosslinking of PIM without crosslinkers

[0180] PIM-13 dissolved in THF at a concentration of 6 mg/mL. Solution was divided into three vials that were exposed to four 370 nm UV lamps for a total of 60 min. A UV-vis spectrum was collected for the material before exposure, and every 15 min, up to 60 min. Qualitatively, the solutions remained yellow over this UV exposure period and no change to the chromophore was observed by UV-vis, when measuring the absorbance profile. See FIG. 6.

[0181] At the 60 min time, the sample was prepared for size exclusion chromatography (SEC) by filtering through a 0.45 um syringe filter. The aliquot was injected into the SEC instrument with a chloroform stationary phase, with columns connected in series, at 40 °C and 0.5 mL/min flow rate. Over this UV exposure period, a molecular weight loss was observed where the PIM-13 M_w began at 72.2 kg/mol and decreased to 36.0 kg/mol. With these long UV dose conditions, the polymer undergoes chain scission reactions resulting in a decrease in molecular weight.

UV Photobleaching Samples				
Sample	Mn (kg/mol)	Mw (kg/mol)	Mz (kg/mol)	PDI
Pristine PIM-13	15.6	72.3	224	4.62
1 h 370nm exposure, 6 mg/mL	18.3	36.0	68.9	1.96
1 h 370nm exposure, 60 mg/mL	17.5	32.9	121	1.88

Example 2: PIM Crosslinking at Different UV Wavelength

[0182] Bench-scale crosslinking and solubility testing was carried out with PIM-DAA and Trimethylolpropane tris(3-mercaptopropionate) ("Trithiol", 33007-83-9). The UV-vis

absorbance spectrum for a PIM polymer is below, with the available lamp wavelengths, supplied by Kessel, marked with vertical lines. See FIG. 7.

[0183] Selecting a 370 nm Kessel PR160L was expected to provide the most light for crosslinking reactions. A second lamp with a 440 nm wavelength was also tested to determine if the polymer absorbance would interfere with crosslinking reactions. Coatings were generated by coating a solution of PIM-DAA (1), trithiol (25 mol%), and DMPA (2.5 mol%) at 60 mL/mL in 1,3-dioxolane onto a 12 µm thick polyethylene battery separator with an 8 µm Meyer Rod. 14 mm diameter punches of these coatings were then irradiated by one of the two lamps. Solubility of the crosslinked film was measured directly after the UV exposure (200 mW/cm^2 * 10 s = 2,000 mJ/cm^2). A second 14 mm punch was prepared with identical conditions and stored in the dark for 24 h to allow the crosslinking reaction to proceed after the UV exposure. Solubility was measured by immersing two punches in 2 mL of chloroform, letting the mixture sit for 24 hours, and measuring the UV-Vis absorbance of the chloroform at 435 nm. Lower UV-vis absorbance values, at 435 nm, indicate less polymer is soluble in chloroform (generally a good solvent for PIMs) and the crosslinking reaction reached a higher conversion. The table below shows the results of the resulting solubility:

Table 2A: Optimum UV Wavelength for Crosslinking PIMs

Example	0d Cure Chloroform Solubility (abs. 435 nm)	1d Cure Chloroform Solubility (abs. 435 nm)
2-1	0.150	0.137
2-2	0.169	0.189
2-3	1.186	1.126
2-4	0.122	0.132
2-5	0.204	0.258
2-6	1.186	1.137
2-7	0.112	0.103
2-8	0.227	0.280
2-9	1.431	1.044
2-10	0.497	0.230
2-11	0.408	0.453
2-12	1.431	1.044

Table 2B: Crosslinking Conditions for Table 2A

Example	Polymer	Thiol	Mol % SH (olefin basis)	Mol% DMPA (olefin basis)	Lamp Wavelength (nm)*	Lamp Power ($mW.cm^2$)	Irradiation Time (s)
2-1	PIM-DAA	Trithiol	25	0	370	200	10
2-2	PIM-DAA	Trithiol	25	0	370	100	10
2-3	PIM-DAA	Trithiol	25	0	NA	0	0
2-4	PIM-DAA	Trithiol	25	0	440	200	10
2-5	PIM-DAA	Trithiol	25	0	440	100	10
2-6	PIM-DAA	Trithiol	25	0	NA	0	0
2-7	PIM-DAA	Trithiol	25	2.5	370	200	10
2-8	PIM-DAA	Trithiol	25	2.5	370	100	10
2-9	PIM-DAA	Trithiol	25	2.5	NA	0	0
2-10	PIM-DAA	Trithiol	25	2.5	440	200	10
2-11	PIM-DAA	Trithiol	25	2.5	440	100	10
2-12	PIM-DAA	Trithiol	25	2.5	NA	0	0

*Note: 'NA' indicates controls with no UV exposure

Example 3: Preparation of Crosslinked PIM with Thiol + Photointiator

[0184] Coatings were prepared by bench-scale application to a polyethylene separator, followed by crosslinking and solubility testing with a combination of polymers, crosslinkers, crosslinker loadings, additives, and irradiation conditions. Coatings were generated by coating a solution of polymer and crosslinker at 60 mL/mL in 1,3-dioxolane onto a 12 µm thick polyethylene battery separator with an 8 µm Meyer Rod. 14 mm diameter punches of these coatings were then irradiated by a 370 nm Kessel PR160L lamp at 1 inch from the source at the time and intensity specified in the table. This distance from the lamp produces a power output of 200 mW/cm^2. After UV exposure, coated punches were dry due to the heat from the lamp. Solubility was assessed on one set of punches immediately after coating. A second set of irradiated punches were left to sit in the dark to cure for 24 h before their solubility was measured by immersing two of the 14 mm punches in 2 mL of chloroform, letting the mixture soak for 24 hours, and measuring the UV-Vis absorbance of the chloroform at 435 nm. Lower UV-vis absorbance values, at 435 nm, indicate less polymer is soluble in chloroform (a good solvent for dissolving PIMs) and the crosslinking reaction reached a higher conversion. Wettability of the coated separator punches was assessed by

dropping 10 µL of LP57 electrolyte onto the middle of the 14mm punch and measuring the diameter of the punch after the LP57 wetted the punch for 10 min. The separator wettability is expressed as the diameter of the LP57 droplet, in millimeters. The table below shows the results of the resulting solubility:

Table 3A: Solubility Assessment of Crosslinked PIM Coatings Prepared by Bench Coating

Example	0d Cure Chloroform Solubility (abs. 435 nm)	1d Cure Chloroform Solubility (abs. 435 nm)	Wettability (mm)*
5-001	0.12830	0.14075	7
5-002	0.16936	0.15802	NT
5-003	0.39844	0.47907	NT
5-004	0.094	0.090	7
5-005	0.149	0.172	NT
5-006	0.742	0.840	NT
5-008	0.23210	0.34308	11
5-009	0.42145	0.26997	NT
5-010	2.28000	1.16330	NT
5-011	0.13921	0.10642	19
5-012	0.23680	0.20190	NT
5-013	0.86953	0.69288	NT
5-014	0.15701	0.17962	9
5-015	0.28743	0.23533	NT
5-016	0.89660	0.77746	NT
5-017	0.038023	0.04927	9
5-018	0.068715	0.07917	NT
5-019	0.340750	0.35634	NT
5-020	0.112	0.103	7
5-021	0.227	0.280	NT
5-022	1.431	1.044	NT
5-023	0.14830	0.17678	10
5-024	0.51095	0.59725	NT
5-025	0.96899	2.16250	NT

Example	0d Cure Chloroform Solubility (abs. 435 nm)	1d Cure Chloroform Solubility (abs. 435 nm)	Wettability (mm)*
5-026	0.030100	0.10056	19
5-027	0.180380	0.29833	NT
5-028	1.721100	3.06160	NT
5-029	0.08012	0.06936	7
5-030	0.07802	0.15806	NT
5-031	0.77542	0.80696	NT
5-032	0.06939	0.06216	8
5-033	0.13710	0.11180	NT
5-034	1.06410	0.97553	NT
5-035	0.14562	0.087834	13
5-036	0.20965	0.16642	NT
5-037	2.07840	1.26590	NT
5-038	0.22359	0.21334	11
5-039	0.79642	0.52527	NT
5-040	2.54180	2.54440	NT
5-041	0.17553	0.16273	9
5-042	0.17712	0.17904	NT
5-043	1.05630	0.93110	NT
5-044	0.09725	0.06183	9
5-045	0.12440	0.08784	NT
5-046	0.80742	0.73379	NT
5-048	0.90917	0.94958	8
5-049	2.32310	1.51720	NT
5-050	2.88030	2.43270	NT
5-051	0.02461	0.03844	7
5-052	0.03676	0.05609	NT
5-053	0.16769	0.15291	NT
5-054	1.68160	2.02590	10
5-055	1.77960	2.11310	NT
5-056	2.12750	1.78630	NT

Example	0d Cure Chloroform Solubility (abs. 435 nm)	1d Cure Chloroform Solubility (abs. 435 nm)	Wettability (mm)*
5-057	1.35420	1.35220	10
5-058	2.00008	2.20950	NT
5-059	1.88520	2.45060	NT
5-060	0.72990	0.75422	11
5-061	0.96214	0.91894	NT
5-062	1.19260	1.07110	NT
5-063	0.24557	0.21497	8
5-064	0.29136	0.24578	NT
5-065	0.70598	0.54875	13
5-066	0.13326	0.10612	15
5-067	0.16654	0.15764	NT
5-068	0.38110	0.35461	10
5-069	0.11971	0.09288	7
5-070	0.28768	0.18559	NT
5-071	0.61296	0.35307	6
5-072	0.05520	0.01724	14
5-073	0.06214	0.02849	NT
5-074	0.13882	0.10400	8
5-075	0.08795	NT	13
5-076	0.13389	NT	NT
5-077	0.73125	NT	NT
5-078	0.14591	0.13997	15
5-079	0.34333	0.20733	NT
5-080	0.98148	1.11310	NT
5-080	0.04724	0.05695	13
5-081	0.06152	0.06628	NT
5-082	0.59370	0.55556	NT
5-083	0.09028	0.10270	14
5-084	0.12269	0.16163	NT
5-085	1.10320	0.73820	NT

Example	0d Cure Chloroform Solubility (abs. 435 nm)	1d Cure Chloroform Solubility (abs. 435 nm)	Wettability (mm)*
5-086	0.19669	0.27717	9
5-087	0.29486	0.42617	NT
5-088	1.08560	1.85240	NT
5-089	0.08968	0.14066	11
5-090	0.11184	0.46275	NT
5-091	0.46726	0.75679	NT
5-092	0.09193	0.13179	19
5-093	0.14845	0.19869	NT
5-094	0.58961	0.95554	NT
5-095	0.03599	0.07665	19
5-096	0.08041	0.09373	14
5-097	0.07040	0.60491	10
5-098	0.19420	0.19086	9
5-099	0.24449	0.22587	NT
5-100	0.69629	0.63917	7
5-101	0.20927	0.13723	12
5-102	0.31288	0.30905	NT
5-103	1.05900	0.83171	10
5-104	0.08765	0.11281	NT
5-105	0.10241	0.17373	NT
5-106	0.31158	0.45475	NT
5-107	0.11320	0.19245	18
5-108	0.19869	0.23523	NT
5-109	0.41547	0.43542	14
5-110	0.39143	0.36630	9
5-111	0.55374	0.54997	NT
5-112	1.05250	0.97928	NT
5-113	0.17946	0.22849	8
5-114	0.32303	0.26216	NT
5-115	1.28220	0.90302	NT

Example	0d Cure Chloroform Solubility (abs. 435 nm)	1d Cure Chloroform Solubility (abs. 435 nm)	Wettability (mm)*
5-116	0.39423	0.41092	14
5-117	0.53217	0.57718	NT
5-118	1.28670	1.29990	NT
5-119	0.18443	0.18452	19
5-120	0.26255	0.27604	NT
5-121	0.80374	0.81955	NT
5-122	0.54307	0.56855	8
5-123	0.74842	0.87205	NT
5-124	2.49430	2.79720	NT
5-125	0.38095	NT	NT
5-126	0.56365	NT	NT
5-127	1.18550	NT	NT
5-128	0.52828	NT	NT
5-129	0.80688	NT	NT
5-130	1.80870	NT	NT
5-131	0.52828	NT	NT
5-132	0.80688	NT	NT
5-133	1.80870	NT	NT
5-134	0.82728		15
5-135	0.98720		
5-136	1.39920		12

*NT: Not Tested

Table 3B: Crosslinking Conditions for Solubility Assessment of Crosslinked PIM Coatings Prepared by Bench Coating

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-001	PIM-DAA (2)	Dithiol	25	0	None	0	200	10
5-002							100	10
5-003							0	0
5-004	PIM-DAA (2)	Trithiol	25	0	None	0	200	10
5-005							100	10
5-006							0	0
5-008	PIM-DAA (2)	Tetra(ethylene glycol) dithiol	25	0	None	0	200	10
5-009							100	10
5-010							0	0
5-011	PIM-DAA (2)	Hexa(ethylene glycol) dithiol	25	0	None	0	200	10
5-012							100	10
5-013							0	0
5-014	PIM-DAA (2)	Hexathiol	25	0	None	0	200	10
5-015							100	10
5-016							0	0
5-017	PIM-DAA (2)	Dithiol	25	2.5	None	0	200	10
5-018							100	10
5-019							0	0
5-020	PIM-DAA (2)	Trithiol	25	2.5	None	0	200	10
5-021							100	10
5-022							0	0

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-023	PIM-DAA (2)	Dithiol	50	0	Trimethylolpropane triacrylate	2.5	200	10
5-024							100	10
5-025							0	0
5-026	PIM-DAA (2)	Dithiol	50	2.5	Trimethylolpropane triacrylate	2.5	200	10
5-027							100	10
5-028							0	0
5-029	PIM-DAA (2)	Dithiol	50	0	Pentaerithitol tetraacrylate	2.5	200	10
5-030							100	10
5-031							0	0
5-032	PIM-DAA (2)	Dithiol	50	2.5	Pentaerithitol tetraacrylate	2.5	200	10
5-033							100	10
5-034							0	0
5-035	PIM-DAA (2)	Trithiol	25	0	Trimethylolpropane triacrylate	5	200	10
5-036							100	10
5-037							0	0
5-038	PIM-DAA (2)	Trithiol	25	0	Pentaerithitol tetraacrylate	5	200	10
5-039							100	10
5-040							0	0
5-041	PIM-DAA (2)	Trithiol	25	0	Acryloylmorpholine	5	200	10
5-042							100	10
5-043							0	0

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-044	PIM-DAA (2)	Trithiol	50	0	Trimethylolpropane triacrylate	2.5	200	10
5-045							100	10
5-046							0	0
5-048	PIM-DAA (2)	Trithiol	50	0	Acryloyl morpholine	2.5	200	10
5-049							100	10
5-050							0	0
5-051	PIM-DAA (2)	Trithiol	50	0	N-vinylimidazole	2.5	200	10
5-052							100	10
5-053							0	0
5-054	PIM-13 / MAA (50/50) (8)	Dithiol	25	0	None	0	200	10
5-055							100	10
5-056							0	0
5-057	PIM-13 / MAA (50/50) (8)	Dithiol	25	0	None	0	200	10
5-058							100	10
5-059							0	0
5-060	PIM-13 / MAA (50/50) (8)	Dithiol	25	0	None	0	200	10
5-061							100	10
5-062							0	0
5-063	PIM-13 / DAA (10/90) (3)	Dithiol	25	0	None	0	200	10
5-064							100	10
5-065							0	0
5-066	PIM-13 / DAA	Trithiol	25	0	None	0	200	10
5-067							100	10

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-068	(10/90) (3)						0	0
5-069	PIM-13 / DAA (10/90) (3)	Dithiol	50	0	None	0	200	10
5-070							100	10
5-071							0	0
5-072	PIM-13 / DAA (10/90) (3)	Trithiol	50	0	None	0	200	10
5-073							100	10
5-074							0	0
5-075	PIM-13 / DAA (10/90) (3)	Dithiol	25	5	None	0	200	10
5-076							100	10
5-077							0	0
5-078	PIM-13 / DAA (10/90) (3)	Trithiol	25	5	None	0	200	10
5-079							100	10
5-080							0	0
5-080	PIM-13 / DAA (10/90) (3)	Dithiol	50	2.5	None	0	200	10
5-081							100	10
5-082							0	0
5-083	PIM-13 / DAA (10/90) (3)	Trithiol	50	2.5	None	0	200	10
5-084							100	10
5-085							0	0
5-086	PIM-13 / DAA	Dithiol	25	5	Trimethylolpropane	5	200	10
5-087							100	10

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-088	(10/90) (3)				triacrylate		0	0
5-089	PIM-13 / DAA (10/90) (3)	Trithiol	25	5	Trimethylolpropane triacrylate	5	200	10
5-090							100	10
5-091							0	0
5-092	PIM-13 / DAA (10/90) (3)	Dithiol	50	2.5	Trimethylolpropane triacrylate	2.5	200	10
5-093							100	10
5-094							0	0
5-095	PIM-13 / DAA (10/90) (3)	Trithiol	50	2.5	Trimethylolpropane triacrylate	2.5	200	10
5-096							100	10
5-097							0	0
5-098	PIM-13 / DAA (20/80) (4)	Dithiol	25	0	None	0	200	10
5-099							100	10
5-100							0	0
5-101	PIM-13 / DAA (20/80) (4)	Trithiol	25	0	None	0	200	10
5-102							100	10
5-103							0	0
5-104	PIM-13 / DAA (20/80) (4)	Dithiol	50	0	None	0	200	10
5-105							100	10
5-106							0	0
5-107	PIM-13 / DAA	Trithiol	50	0	None	0	200	10
5-108							100	10

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-109	(20/80) (4)						0	0
5-110	PIM-13 / DAA (20/80) (4)	Cyclohexane-1,4-diyl bis(3-mercaptopropanoate)	25	0	None	0	200	10
5-111							100	10
5-112							0	0
5-113	PIM-13 / DAA (20/80) (4)	Cyclohexane-1,4-diyl bis(3-mercaptopropanoate)	50	2.5	None	0	200	10
5-114							100	10
5-115							0	0
5-116	PIM-13 / DAA (20/80) (4)	Cyclohexane-1,4-diyl bis(3-mercaptopropanoate)	25	5	None	0	200	10
5-117							100	10
5-118							0	0
5-119	PIM-13 / DAA (20/80) (4)	Cyclohexane-1,4-diyl bis(3-mercaptopropanoate)	50	2.5	Trimethylolpropane triacrylate	2.5	200	10
5-120							100	10
5-121							0	0
5-122	PIM-13 / DAA (20/80) (4)	Cyclohexane-1,4-diyl bis(3-mercaptopropanoate)	25	5	Trimethylolpropane triacrylate	5	200	10
5-123							100	10
5-124							0	0
5-125	PIM-13 / DAA (20/80) (4)	Di(ethylene glycol) bis 3-mercaptopropionate	25	0	None	0	200	10
5-126							100	10
5-127							0	0
5-128	PIM-13 / DAA	Tri(ethylene glycol) bis 3-	25	0	None	0	200	10
5-129							100	10

Ex.	Polymer	Crosslinker	Mol% Cross-linker	Mol% DMPA Initiator	Additive	Mol% Additive	Lamp Power (mW/cm^2)	Irradiation Time (s)
5-130	(20/80) (4)	mercaptopropionate					0	0
5-131	PIM-13 / DAA (20/80) (4)	Tetra(ethylene glycol) bis 3-mercaptopropionate	25	0	None	0	200	10
5-132							100	10
5-133							0	0
5-134	PIM-13 / DAA (50/50)	Tris|2-(3-mercaptopropionyloxy)ethyl] isocyanurate	25	2.5	None	0	200	10
5-135							100	10
5-136							0	0

Example 4: Preparation of Crosslinked PIMs by R2R Coating Methods

[0185] The coating solution (also called the "ink" herewith) was prepared by stirring the polymer in 1,3-dioxolane at 60 mg/mL, for at least 4 h, followed by filtration through a 1 µm pore glass fiber syringe filter. The solids content of the ink is based on the thickness and porosity of the base separator and the desired weight of the coating. The ink was applied to the base polyethylene separators through a roll-to-roll (R2R) coating process using a slot die head to apply the ink. Solubility was assessed on one set of punches with and without UV exposure, immediately after coating. These irradiated coating rolls were left to sit in the dark to cure for 24 h before their solubility was measured by immersing two of the 14 mm punches in 2 mL of chloroform, letting the mixture sit for 24 hours, and measuring the UV-Vis absorbance of the chloroform at 435 nm. Absorbance of the UV-crosslinked film was compared to a section of the film with no UV exposure to calculate the % solubility due to UV exposure and 24 h cure time. Lower UV-vis absorbance values, at 435 nm, indicate less polymer is soluble in chloroform (a good solvent for dissolving PIMs) and the crosslinking reaction reached a higher conversion.

[0186] Coating weights were measured by measuring the mass of a 10 cm x 10 cm punch of the coated separator and subtracting the mass of a 10 x 10 punch of the base separator. Coat weights for these coatings were maintained below 1.0 g/m^2. A Gurley densometer

(Gurley Precision Instruments Model #4150N) was used to measure air permeability through the coated separators, as described in the ASTM D726 and TAPPI T-536-88 ("Resistance of Paper to Passage of Air) high pressure Gurley. A typical uncoated polyethylene separator has a Gurley value of ~90 s/100mL air. Gurley values of >10,000 suggest that a coating is conformal on the separator surface and free of pinhole defects.

[0187] The average heat shrinkage (%, ASTM D1204) at 150°C for 1 h, by averaging the shrinkage measured for punches in the machine direction (MD) and transverse direction (TD). A 45 mm x 50 mm punch is taken and a 40 mm x 45 mm rectangle is drawn on the punch in pen. The sample is sandwiched between 10 sheets of A4 paper and heated to 150°C for 1 h. Dimensions of the rectangle are measured and the % heat shrinkage is calculated. Heat shrinkage is key in assessing the thermal stability of battery separator materials. This measurement is conducted for dry separator samples and separator samples that have been soaked in electrolyte consisting of lithiumpentafluorophosphate (LP57, 1 mol/L), dissolved in ethylene carbonate (EC, 3 parts by mass) and ethyl methyl carbonate (EMC, 7 parts by mass).

[0188] Multilayer lithium ion cells were prepared on a semi-automated puncher-stacker (EnergyTech Solutions) in a 2 cathode/3 anode format, with welded tabs and heat-sealed pouches. All cell level test used LP57 (1M $LiPF_6$ dissolved in 3 parts ethylene carbonate to 7 parts ethyl methyl carbonate), NMC631 cathodes, and graphite anodes. A slow formation protocol was used to passivate electrodes and prepare the cells for testing, similar to the slow formation used by Schomburg and coworkers (Schomburg, F., et al., Energy Environ. Sci., 2024, 17, 2686). After formation, cells under a hybrid pulse power characterization (HPPC) for charge and discharge at 100% depth of discharge. The first step in the HPPC protocol is a C/3 charge and D/3 discharge where the "1st Cycle Coulombic Efficiency" calculated from the ratio of discharge and charge capacities. Resistance is calculated from the potential and current changes on 1C pulses to yield the "10s Discharge Pulse Resistance at 1C Rate" expressed in $\Omega.cm^2$ (Bialon, T., *et al.*, *Energies*, 2023, 16(17), 6239.).

Table 4A: Coating Parameters and Cell Testing Results for R2R Coating Method

Ex	PIM Solubility (mass%)	Coat Weight (g/m^2)	Gurley ($s/100cm^3$)	Average Heat Shrinkage (%)	1st Cycle Coulombic Efficiency (%)	10 s Discharge Pulse Resistance at 1C Rate ($\Omega.cm^2$)
Control	NA	NA	90	75	95.4	24.1
6-001	6.9	0.76	137,574	NT	15.4	56.7

Ex	PIM Solubility (mass%)	Coat Weight (g/m^2)	Gurley ($s/100cm^3$)	Average Heat Shrinkage (%)	1st Cycle Coulombic Efficiency (%)	10 s Discharge Pulse Resistance at 1C Rate ($\Omega.cm^2$)
6-002	13.8	0.76	137,574	NT	22.4	73.1
6-003	7.0	0.80	156,188	19.3	57.8	54.0
6-004	10.2	0.80	>10,000	17.6	39.7	58.1
6-005	16.4	0.81	>10,000	18.6	38.2	62.7
6-006	3.0	0.83	>10,000	13.7	31.6	61.9
6-007	3.3	0.62	31,860	32.1	68.4	45.0
6-008	3.0	0.76	648,900	39.7	50.6	51.9
6-009	4.2	0.82	110,400	28.8	55.2	54.7
6-010	2.9	0.55	1,242,000	25.7	45.0	54.2
6-011	6.4	0.55	1,242,000	12.8	54.8	64.9
6-012	3.3	0.86	3,643,200	1.8	41.4	42.7
6-013	4.6	0.82	>10,000	16.9	53.8	49.5
6-014	5.9	0.71	1,729,638	17.5	Test failure - resistance too high to measure.	
6-015	8.6	0.72	102,708	16.7	26.0	58.9
6-016	7.1	0.68	3,464,856	21.7	28.7	60.4
6-017	4.5	0.66	850,176	13.6	34.5	57.5
6-018	10.1	0.67	2,557,026	17.0	26.3	51.0
6-019	15.1	0.59	10,173,379	NT	NT	NT
6-020	10.8	0.79	1,987,200	36.9	33.0	45.6
6-021	8.6	0.74	1,987,200	16.1	38.9	48.7
6-022	11.2	0.69	1,902,402	13.6	55.2	34.2

Table 4B: Crosslinking and Coating Conditions for Coating Parameters and Cell Testing Results for R2R Coating Method

Ex. No.	Polymer	Crosslinker	Mol% Crosslinker	Mol% DMPA	Additive	Mol% Additive	UV Line Speed (m/min)	Base Layer Thickness (µm)
Control	Uncoated Polyethylene Control Separator							9
6-001	PIM-DAA	Trithiol	30	5	None	0	0.5	9
6-002	PIM-DAA	Trithiol	30	5	None	0	1.0	9
6-003	PIM-DAA	Trithiol	30	0	None	0	0.1	12
6-004	PIM-DAA	Dithiol	30	5	None	0	0.5	12
6-005	PIM-DAA	Dithiol	30	5	Triacrylate	5	0.5	12
6-006	PIM-DAA	Trithiol	30	5	Triacrylate	5	0.1	9

Ex. No.	Polymer	Crosslinker	Mol% Crosslinker	Mol% DMPA	Additive	Mol% Additive	UV Line Speed (m/min)	Base Layer Thickness (µm)
6-007	PIM-DAA	Trithiol	30	2.5	None	0	0.1	12
6-008	PIM-13/DAA (10/90)	Trithiol	30	5	None	0	0.1	12
6-009	PIM-13/DAA (10/90)	Trithiol	30	5	Triacrylate	2.5	0.1	12
6-010	PIM-DAA	Trithiol	30	10	None	0	0.1	12
6-011	PIM-DAA	Trithiol	30	10	None	0	0.5	12
6-012	PIM-13/DAA (20/80)	Trithiol	30	5	None	0	0.1	12
6-013	PIM-13/DAA (20/80)	Trithiol	30	5	Triacrylate	5	0.1	9
6-014	PIM-DAA	CD-BMP	30	5	None	0	0.1	9
6-015	PIM-DAA	2EG-BMP	30	5	None	0	0.1	9
6-016	PIM-DAA	3EG-BMP	30	5	None	0	0.1	9
6-017	PIM-DAA	4EG-BMP	30	5	None	0	0.1	9
6-018	PIM-13/DAA (20/80)	CD-BMP	30	5	None	0	0.1	9
6-019	PIM-13/DAA (20/80)	2EG-BMP	30	5	None	0	0.1	9
6-020	PIM-13/DAA (20/80)	3EG-BMP	30	5	None	0	0.1	9
6-021	PIM-13/DAA (20/80)	4EG-BMP	30	5	None	0	0.1	9
6-022	PIM-13/DAA (30/70)	Trithiol	30	5	None	0	0.1	9

[0189] Bench-scale crosslinking and solubility testing with a combination of polymers, crosslinkers, crosslinker loadings, and irradiation conditions. Coatings were generated by coating a solution of polymer and crosslinker at 60 mL/mL in 1,3-dioxolane onto a 12 µm thick polyethylene battery separator with an 8 µm Meyer Rod. 14 mm diameter punches of

these coatings were then irradiated by a 370 nm Kessel PR160L lamp at 1 inch from the source at the time and intensity specified in Table 1. These irradiated punches were left to sit in the dark to cure at various times specified in the table before their solubility was measured by immersing two punches in 2 mL of chloroform, letting the mixture sit for 24 hours, and measuring the UV-Vis absorbance of the chloroform at 435 nm.

Table 5A: Crosslinked PIMs Reaction Conditions

Ex. No.	Polymer	Thiol	Mol % SH (olefin basis)	Lamp Intensity (%)	Irradiation Time (s)
1-1	PIM-DAA	Tetra-Thiol	25	100	10
1-2	PIM-DAA	Tetra-Thiol	25	100	5
1-3	PIM-DAA	Tetra-Thiol	25	25	5
1-4	PIM-DAA	Tetra-Thiol	25	0	0
2-1	PIM-DAA	Tri-Thiol	25	100	10
2-2	PIM-DAA	Tri-Thiol	25	100	5
2-3	PIM-DAA	Tri-Thiol	25	25	5
2-4	PIM-DAA	Tri-Thiol	25	0	0
3-1	PIM-DAA	Di-Thiol	25	100	10
3-2	PIM-DAA	Di-Thiol	25	100	5
3-3	PIM-DAA	Di-Thiol	25	25	5
3-4	PIM-DAA	Di-Thiol	25	0	0
4-1	PIM-DAA	Tetra-Thiol	12.5	100	10
4-2	PIM-DAA	Tetra-Thiol	12.5	100	5
4-3	PIM-DAA	Tetra-Thiol	12.5	25	5
4-4	PIM-DAA	Tetra-Thiol	12.5	0	0
5-1	PIM-DAA	Tri-Thiol	12.5	100	10
5-2	PIM-DAA	Tri-Thiol	12.5	100	5
5-3	PIM-DAA	Tri-Thiol	12.5	25	5
5-4	PIM-DAA	Tri-Thiol	12.5	0	0
6-1	PIM-DAA	Di-Thiol	12.5	100	10
6-2	PIM-DAA	Di-Thiol	12.5	100	5
6-3	PIM-DAA	Di-Thiol	12.5	25	5
6-4	PIM-DAA	Di-Thiol	12.5	0	0
7-1	PIM-AA	Tri-Thiol	25	100	10
7-2	PIM-AA	Tri-Thiol	25	100	5
7-3	PIM-AA	Tri-Thiol	25	25	5

Ex. No.	Polymer	Thiol	Mol % SH (olefin basis)	Lamp Intensity (%)	Irradiation Time (s)
7-4	PIM-AA	Tri-Thiol	25	0	0
8-1	PIM-AA	Di-Thiol	25	100	10
8-2	PIM-AA	Di-Thiol	25	100	5
8-3	PIM-AA	Di-Thiol	25	25	5
8-4	PIM-AA	Di-Thiol	25	0	0
9-1	PIM-13/ MAA (50/50)	Tri-Thiol	50	100	10
9-2	PIM-13/ MAA (50/50)	Tri-Thiol	50	100	5
9-3	PIM-13/ MAA (50/50)	Tri-Thiol	50	25	5
9-4	PIM-13/ MAA (50/50)	Tri-Thiol	50	0	0

Table 5B: Crosslinked PIMs Characterization

Ex. No.	0d Cure CHCl3 sol. (abs. 435 nm)	1d Cure CHCl3 sol. (abs. 435 nm)	2d Cure CHCl3 sol. (abs. 435 nm)	7d Cure CHCl3 sol. (abs. 435 nm)	8d Cure CHCl3 sol. (abs. 435 nm)
1-1	0.39018	0.28815	0.31242		0.23868
1-2	0.54270	0.44721	0.37106		0.33234
1-3	1.18410	0.84853	1.36400		
1-4	1.65310	1.63650	1.40240		1.069
2-1	0.20324	0.17211	0.24551		0.20157
2-2	0.37227	0.35289	0.29787		0.31104
2-3	1.05630	0.91741	0.91759		0.65696
2-4	1.46920	1.39560	1.21310		1.0333
3-1	0.24634	0.24733	0.37463		0.33142
3-2	0.38807	0.32985	0.45343		0.32725
3-3	0.54972	0.60924	0.58850		0.63326
3-4	0.90351	0.99767	1.02490		1.1018
4-1	0.62445	0.38594	0.42410		0.47841
4-2	0.55317	0.56983	0.67923		0.57459
4-3	0.98547	0.83934	0.97531		0.866
4-4	1.05190	1.25620	1.27300		1.1854
5-1	0.36585	0.30013	0.35331		0.34524
5-2	0.46236	0.46898	0.49869		0.44051

Ex. No.	0d Cure CHCl3 sol. (abs. 435 nm)	1d Cure CHCl3 sol. (abs. 435 nm)	2d Cure CHCl3 sol. (abs. 435 nm)	7d Cure CHCl3 sol. (abs. 435 nm)	8d Cure CHCl3 sol. (abs. 435 nm)
5-3	0.85098	0.72944	0.92012		0.57696
5-4	1.23840	1.17500	1.14920		0.80845
6-1	0.48697	0.47966	0.43752		0.43957
6-2	0.54050	0.51570	0.60866		0.47044
6-3	0.75660	0.82300	0.76669		0.86434
6-4	1.09950	1.08230	1.02560		1.2219
7-1	0.56607		0.62624	0.56639	
7-2	0.64279		0.86919	0.77387	
7-3	1.29230		1.0784	1.0241	
7-4	1.45960		1.5916	1.2947	
8-1	0.65463		0.61402	0.68915	
8-2	0.62659		0.68917	0.64771	
8-3	1.00020		0.98159	0.9436	
8-4	1.49150		1.3832	0.99791	
9-1	1.3062	0.94145	1.1848		
9-2	1.1799	1.1118	1.1387		
9-3	1.9011	1.5899	1.7965		
9-4	1.7115	1.8315	1.7711		

[0190] Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, one of skill in the art will appreciate that certain changes and modifications may be practiced within the scope of the appended claims. In addition, each reference provided herein is incorporated by reference in its entirety to the same extent as if each reference was individually incorporated by reference. Where a conflict exists between the instant application and a reference provided herein, the instant application shall dominate.

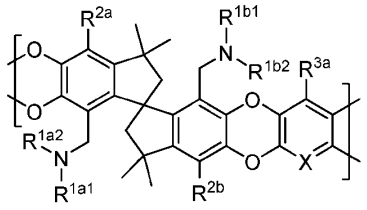
WHAT IS CLAIMED IS:

1. A cross-linkable polymer composition comprising:

a polymer of Formula (I):

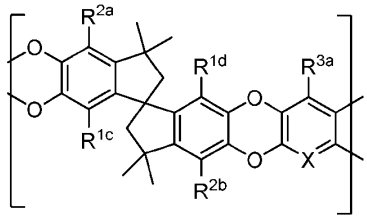
$$[A]_n\text{-}[B]_m \quad (I) \quad ,$$

wherein each repeat unit A independently has the structure of Formula A-I:



(A-I) ,

and each repeat unit B independently has the structure of Formula B-I:



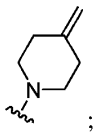
(B-I) ,

and a crosslinker,

wherein

each R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

at least two of R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are C_{2-6} alkenyl, or R^{1a1} and R^{1a2}, and R^{1b1} and R^{1b2}, are combined with the atoms to which they are attached to form:



;

R^{1c} and R^{1d} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1e}$ or $NR^{1c1}R^{1d1}$;

each R^{1c1} and R^{1d1} are independently hydrogen, C_{1-6} alkyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1c2}R^{1d2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1c2} and R^{1d2} is independently hydrogen or C_{1-6} alkyl;

each R^{1e} is independently $NR^{1c2}R^{1d2}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1f} groups;

each R^{1f} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{1f1}$, $–C(O)OR^{1f1}$, $–S(O)_2R^{1f1}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{1f1})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1f1} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CH_2R^{2c} or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, –$C(O)R^{2e}$, $–C(O)OR^{2e}$, $–S(O)_2R^{2e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or $–C(R^{3b})$=;

each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or $–S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl;

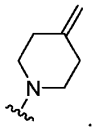
subscript n is an integer from 10 to 10,000; and

subscript m is an integer from 0 to 10,000.

2. The cross-linkable polymer composition of claim 1, wherein

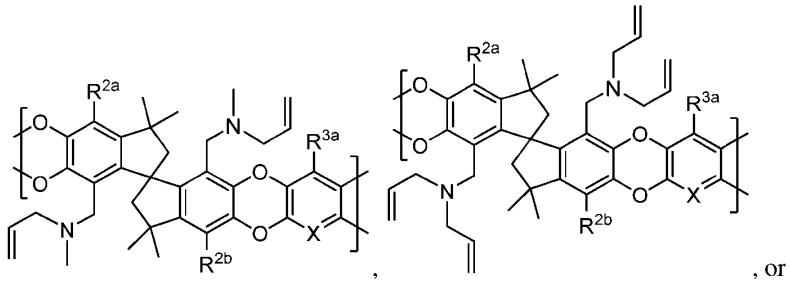
each R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} are independently C_{1-6} alkyl, or C_{2-6} alkenyl; and

at least one of R^{1a1}, R^{1a2}, R^{1b1} and R^{1b2} is C_{2-6} alkenyl, or R^{1a1} and R^{1a2}, and R^{1b1} and R^{1b2}, are combined with the atoms to which they are attached to form:

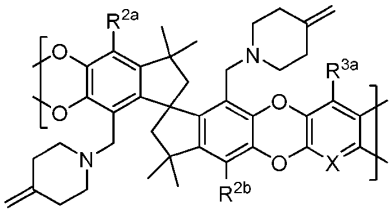


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3. The cross-linkable polymer composition of claim 1, wherein each repeat unit A independently has the structure:



, or



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4. The cross-linkable polymer composition of claim 1, wherein subscript m is 0.

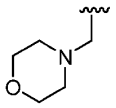
5. The cross-linkable polymer composition of claim 1, wherein subscript m is an integer from 1 to 10,000.

6. The cross-linkable polymer composition of claim 1, wherein

R^{1c} and R^{1d} are each independently $-CH_2R^{1e}$; and

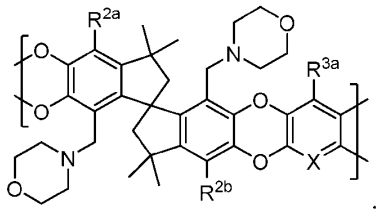
each R^{1e} is independently a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S.

7. The cross-linkable polymer composition of claim 1, wherein R^{1c} and R^{1d} are each



.

8. The cross-linkable polymer composition of claim 1, wherein each repeat unit B independently has the structure:



.

9. The cross-linkable polymer composition of claim 1, wherein the molar ratio of repeat unit A to repeat unit B is about 5:95, 10:90, 15:85, 20:80, 25:75, 30:70, 35:65, 40:60, 45:55, 50:50, 55:45, 60:40, 65:45, 70:30, 75:25, 80:20, 85:15, 90:10, or 95:5.

10. The cross-linkable polymer composition of claim 1, wherein the molar ratio of repeat unit A to repeat unit B is about 50:50.

11. The cross-linkable polymer composition of claim 1, wherein R^{2a} and R^{2b} are each hydrogen.

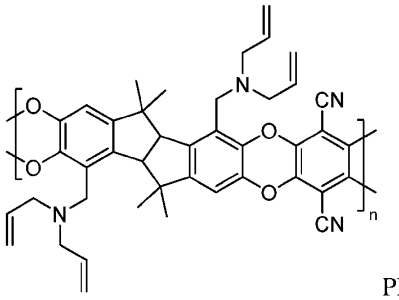
12. The cross-linkable polymer composition of claim 1, wherein

R^{3a} is –CN;

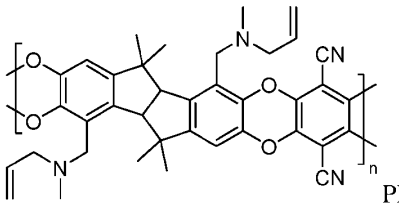
X is $-C(R^{3b})=$; and

R^{3b} is –CN.

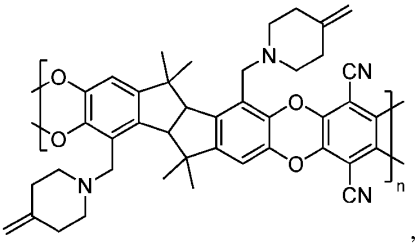
13. The cross-linkable polymer composition of claim 1, wherein the polymer of Formula (I) is:



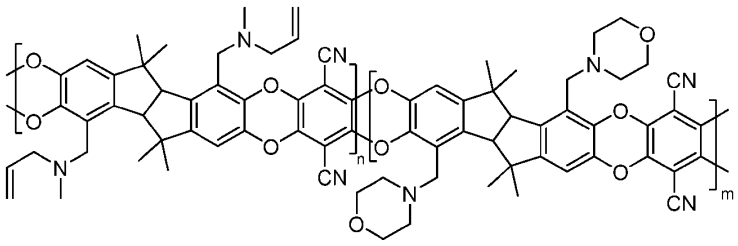
PIM-DAA,



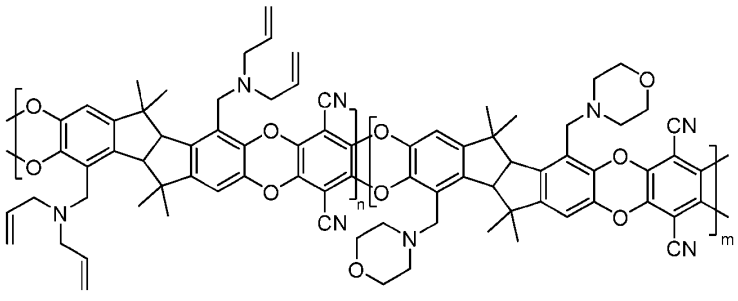
PIM-MAA,



,



PIM-13/PIM-MAA, or



PIM-13/PIM-DAA.

14. The cross-linkable polymer composition of claim 1, wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from about 1 kg/mol to 1000 kg/mol.

15. The cross-linkable polymer composition of claim 1, wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from about 10 kg/mol to 500 kg/mol.

16. The cross-linkable polymer composition of claim 1, wherein the weight average molecular weight (M_w) of the polymer of Formula (I) is from about 35 kg/mol to 250 kg/mol.

17. The cross-linkable polymer composition of claim 1, wherein the crosslinker is a dithiol, trithiol, tetrathiol, pentathiol, or hexathiol.

18. The cross-linkable polymer composition of claim 1, wherein the crosslinker is 2,2'-(ethylenedioxy)diethanethiol, trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), dipentaerithritol hexakis(3-mercaptopropionate), tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate, dipentaerythritol hexakis(3-mercaptopropionate), hexa(ethylene glycol) dithiol, 1,11-dimercapto-3,6,9-trioxaundecane, cyclohexane-1,4-diyl bis(3-mercaptopropanoate), di(ethylene glycol) bis(3-mercaptopropionate), tri(ethylene glycol) bis(3-mercaptopropionate), or tetra(ethylene glycol) bis(3-mercaptopropionate).

19. The cross-linkable polymer composition of claim 1, wherein the crosslinker is 2,2'-(ethylenedioxy)diethanethiol, trimethylolpropane tris(3-mercaptopropionate), or pentaerythritol tetrakis(3-mercaptopropionate).

20. The cross-linkable polymer composition of claim 1, wherein the crosslinker is present in an amount of from about 5 to 75 mol% relative to the polymer of Formula (I).

21. The cross-linkable polymer composition of claim 1, wherein the crosslinker is present in an amount of from about 12.5 to 50 mol% relative to the polymer of Formula (I).

22. The cross-linkable polymer composition of claim 1, wherein the crosslinker is present in an amount of about 12.5, 25, or 50 mol% relative to the polymer of Formula (I).

23. The cross-linkable polymer composition of claim 1, further comprising a solvent.

24. The cross-linkable polymer composition of claim 23, wherein the solvent comprises water, 1,3-dioxolane, tetrahydrofuran, or N-methylpyrrolidone, or a combination thereof.

25. The cross-linkable polymer composition of claim 23, wherein the polymer of Formula (I) and crosslinker are at a concentration of from about 10 to 100 mL/mL in the solvent.

26. The cross-linkable polymer composition of claim 23, wherein the polymer of Formula (I) and crosslinker are at a concentration of about 60 mL/mL in the solvent.

27. The cross-linkable polymer composition of claim 1, further comprising a photoinitiator.

28. The cross-linkable polymer composition of claim 27, wherein the photoinitiator comprises acetophenone, anisoin, anthraquinone, anthraquinone-2-sulfonic acid sodium salt monohydrate, benzil, benzoin, benzoin ethyl ether, benzoin isobutyl ether, benzophenone, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4-benzoylbiphenyl, 2-benzyl-2-(dimethylamino)-4'- morpholinobutyrophenone, 4,4'-bis(diethylamino)benzophenone, 4,4'-bis(dimethylamino)benzophenone, camphorquinone, 2-chlorothioxanthen-9-one, (cumene)cyclopentadienyliron(II) hexafluorophosphate, dibenzosuberenone, 2,2-diethoxyacetophenone, 4,4'-dihydroxybenzophenone, 2,2-dimethoxy-2-phenylacetophenone (DMPA), 4-(dimethylamino)benzophenone, 4,4'-dimethylbenzil, 2,5-dimethylbenzophenone, 3,4-dimethylbenzophenone, diphenyl(2,4,6 trimethylbenzoyl)phosphine oxide, 4'-ethoxyacetophenone, ethylanthraquinone, ferrocene, 3'-hydroxyacetophenone, 4'-hydroxyacetophenone, 3-hydroxybenzophenone, 4-hydroxybenzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-

methylpropiophenone, 4-hydroxybenzophenone, 3-methylbenzophenone, methyl benzoylformate, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, phenanthrenequinone, 4'-phenoxyacetophenone, or a combination thereof.

29. The cross-linkable polymer composition of claim 27, wherein the photoinitiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA).

30. The cross-linkable polymer composition of claim 1, further comprising a crosslinking additive.

31. The cross-linkable polymer composition of claim 30, wherein the crosslinking additive comprises alkyl acrylates, methyl acrylate, pentaerythritol tetraacrylate, trimethylolpropane triacrylate, 2,2,2-trifluoroethyl acrylate, 1,1,1,3,3,3-hexafluoroisopropyl acrylate, fluoroalkyl acrylates, pentafluorophenyl acrylate, 2-(dimethylamino)ethyl acrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 2-isocyanatoethyl acrylate, tetrahydrofurfuryl acrylate, 4-acryloylmorpholine, triisopropylsilyl acrylate, 3-[dimethyoxy(methyl)silyl]propyl acrylate, 3-(methoxydimethylsilyl)propyl acrylate, 3-(trimethoxysilyl)propyl acrylate, *N*-succinimidyl acrylate, 2-cyanoethyl acrylate, α-methylene-γ-butyrolactone, (diethoxyphosphoryl)methyl acrylate, oxiran-2-ylmethyl acrylate, 4-hydroxybutyl acrylate glycidyl ether, 2-*N*-morpholinoethyl acrylate, *N*,*N*-dimethylprop-2-en-1-amine, acrylamide, *N*-(isobutoxymethyl)acrylamide, *N*-(2-(pyridin-2-yl)ethyl)acrylamide, *N*-[3-dimethylamino)propyl]methacrylamide, *N*-[2-(dimethylamino)ethyl]methacrylamide, *N*-[3-(dimethylamino)propyl]acrylamide, 2-(diethylamino)ethyl methacrylate, *N*-[2-(5-imidazolyl)ethyl]acrylamide, 1-vinylimidazole, 1-vinyl-1,2,4-triazole, 2-methyl-1-vinylimidazole, 4-vinylpyridine, styrene, 4-(trifluoromethyl)styrene, 4-methoxystyrene, 4-(trifluoromethoxy)styrene, alpha-(trifluoromethyl)styrene, 3,5-bis(trifluoromethyl)styrene, or a combination thereof.

32. The cross-linkable polymer composition of claim 31, wherein the crosslinking additive is pentaerythritol tetraacrylate, trimethylolpropane triacrylate, 4-acryloylmorpholine, *N*,*N*-dimethylprop-2-en-1-amine, or 1-vinylimidazole.

33. A method of preparing a polymer, the method comprising:

a) forming a reaction mixture comprising a cross-linkable polymer composition of any one of claims 1 to 32, under conditions suitable to prepare the polymer.

34. The method of claim 33, further comprising heating the reaction mixture at a temperature of from about 70 °C to 140 °C.

35. The method of claim 33, further comprising irradiating the reaction mixture

at a wavelength of about 370 nm;

at a lamp power of from about 10 to 10,000 mW/cm^2; and

for a time period of from about 0.001 to 100 seconds.

36. The method of claim 35, wherein the irradiating is conducted at a lamp power of about 200 mW/cm^2.

37. The method of claim 35, wherein the irradiating provides a UV dose of from 10 to 10,000 mJ/cm^2.

38. The method of claim 35, wherein the irradiating is conducted for a time period of from 0.001 to 10 seconds .

39. The method of claim 35, wherein the irradiating is conducted for a time period of about 5 or 10 seconds .

40. The method of claim 35, wherein the irradiating is conducted at a wavelength of about 370 nm, for a time period of about 10 seconds, and:

a) at a lamp power of about 200 mW/cm^2; or

b) at a lamp power of about 100 mW/cm^2.

41. The method of claim 35, wherein

the polymer of Formula (I) is PIM-DAA;

the crosslinker is 2,2'-(ethylenedioxy)diethanethiol present in an amount of about 12.5 mol% relative to PIM-DAA;

the solvent is 1,3-dioxolane; and

the irradiating is conducted at a lamp power of about 200 mW/cm^2.

42. The method of claim 35, wherein

the polymer of Formula (I) is PIM-MAA;

the crosslinker is trimethylolpropane tris(3-mercaptopropionate) present in an amount of about 25 mol% relative to PIM-DAA;
the solvent is 1,3-dioxolane; and
the irradiating is conducted at a lamp power of about 200 mW/cm^2.

43. The method of claim 35, wherein
the polymer of Formula (I) is PIM-13/PIM-MAA (50/50) copolymer;
the crosslinker is 2,2'-(ethylenedioxy)diethanethiol present in an amount of about 25 mol% relative to PIM-13/PIM-MAA (50/50);
the solvent is 1,3-dioxolane; and
the irradiating is conducted at a lamp power of about 200 mW/cm^2.

44. The method of claim 35, wherein
the polymer of Formula (I) is PIM-13/PIM-DAA (10/90) copolymer;
the crosslinker is 2,2'-(ethylenedioxy)diethanethiol present in an amount of about 50 mol% relative to PIM-13/PIM-DAA (10/90);
the solvent is 1,3-dioxolane;
the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) present in an amount of about 2.5 mol% relative to PIM-13/PIM-DAA (10/90); and
the irradiating is conducted at a lamp power of about 200 mW/cm^2.

45. The method of claim 35, wherein
the polymer of Formula (I) is PIM-13/PIM-DAA (20/80) copolymer;
the crosslinker is 2,2'-(ethylenedioxy)diethanethiol present in an amount of about 50 mol% relative to PIM-13/PIM-DAA (20/80);
the solvent is 1,3-dioxolane; and
the irradiating is conducted at a lamp power of about 200 mW/cm^2.

46. The method of claim 35, wherein
the polymer of Formula (I) is PIM-13/PIM-DAA (30/70) copolymer;
the crosslinker is trimethylolpropane tris(3-mercaptopropionate) present in an amount of about 30 mol% relative to PIM-13/PIM-DAA (30/70);
the solvent is 1,3-dioxolane;
the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) present in an amount of about 5 mol% relative to PIM-13/PIM-DAA (30/70); and

the irradiating is conducted at a lamp power of about 200 mW/cm^2.

47. The method of claim 35, wherein
the polymer of Formula (I) is PIM-13/PIM-DAA (50/50) copolymer;
the crosslinker is tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate present in an amount of about 25 mol% relative to PIM-13/PIM-DAA (50/50);
the solvent is 1,3-dioxolane;
the photointiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA) present in an amount of about 2.5 mol% relative to PIM-13/PIM-DAA (50/50); and
the irradiating is conducted at a lamp power of about 200 mW/cm^2.

48. The method of claim 33, further comprising: curing the crosslinked polymer by sitting in the dark for 0 to 30 days.

49. The method of claim 33, further comprising prior to crosslinking:
a2) coating a separator with the reaction mixture.

50. A separator prepared by the method of claim 49.

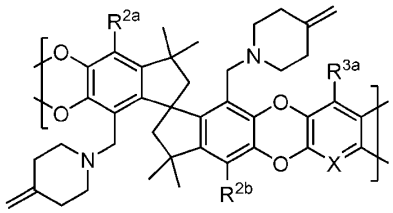
51. A polymer prepared by the method of any one of claims 33 to 49.

52. An electrochemical device comprising
an anode;
a cathode;
a separator between the anode and cathode, wherein the separator is coated on one side with a polymer of claim 51; and
an electrolyte composition.

53. A polymer of Formula (I):

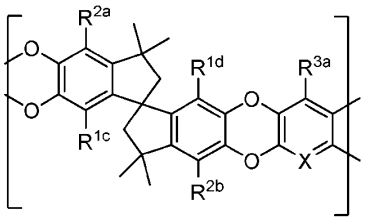
$$[A]_n\text{-}[B]_m \quad (I) \quad ,$$

wherein each repeat unit A has the structure of Formula A-I:



(A-I) ,

and each repeat unit B independently has the structure of Formula B-I:



(B-I) ,

wherein

R^{1c} and R^{1d} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1e}$ or $NR^{1c1}R^{1d1}$;

each R^{1c1} and R^{1d1} are independently hydrogen, C_{1-6} alkyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1c2}R^{1d2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1c2} and R^{1d2} is independently hydrogen or C_{1-6} alkyl;

each R^{1e} is independently $NR^{1c2}R^{1d2}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1f} groups;

each R^{1f} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{1f1}$, $–C(O)OR^{1f1}$, $–S(O)_2R^{1f1}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{1f1})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1f1} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{2c}$ or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl

having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{2e}$, $–C(O)OR^{2e}$, $–S(O)_2R^{2e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or $–C(R^{3b})=$;

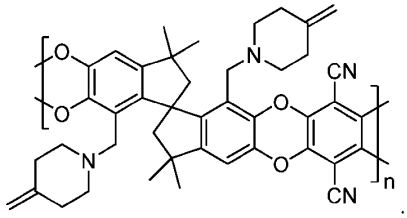
each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or $–S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl;

subscript n is an integer from 10 to 10,000; and

subscript m is an integer from 0 to 10,000.

54. The polymer of claim 53, having the structure:



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