

CHEMICALLY RESISTANT ISOPOROUS CROSSLINKED BLOCK COPOLYMER STRUCTURE

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] This application claims the benefit of priority to United States Provisional Patent Application Serial No. 62/560,452, filed September 19, 2017, the entirety of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] Isoporous block copolymers of cross-linked structures, and methods of preparing, which are resistant to harsh solvent conditions from organic, acidic or basic materials.

BACKGROUND OF THE INVENTION

[0003] Multiblock copolymers used to achieve self-assembled isoporous structures are amenable to generating high flux, solvent-resistant, isoporous materials. Additionally, the nature of block copolymers allows for multi-functionality of the materials, whereas one block can impart significant chemical resistance (if crosslinked, for example) while the other blocks provide other functionalities, e.g. mechanical integrity. These materials are particularly useful as chemically resistant membranes for separations.

[0004] Cross-linking of polymers, block or otherwise, prior to pore formation are known, See for example, Wang et al. (J. Mem. Sci., 476, 2015, 449-456); Decker et al. (Macromol. Chem. Phys. 200, 1999, 1965-1974.); US3864229; US8865841 B2.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] **Figure 1A-1D** are scanning electron images of a crosslinked poly(isoprene)-*b*-poly(styrene)-*b*-poly(4-vinylpyridine) isoporous asymmetric membrane (as described below, in for example, ¶ [0038], before and after (DMF) dimethylformamide exposure).

[0006] **Figure 1A** is the cross-section of the membrane before DMF exposure.

[0007] **Figure 1B** is the selective surface of the material before DMF exposure.

[0008] **Figure 1C** is the cross-section of the material after DMF exposure.

[0009] **Figure 1D** is the selective surface of the material after DMF exposure.

[0010] **Figure 2A-2B** are scanning electron images of a crosslinked poly(isoprene)-*b*-poly(styrene)-*b*-poly(4-vinylpyridine) isoporous asymmetric material (as described below, in for example ¶ [0038] before and after tetrahydrofuran (THF) exposure).

[0011] **Figure 2A** is the selective surface of the material before THF exposure.

[0012] **Figure 3B** is the selective surface of the material after THF exposure.

[0013] **Figure 3A-3D** are scanning electron images of a crosslinked poly(isoprene)-*b*-poly(styrene)-*b*-poly(4-vinylpyridine) isoporous asymmetric material (as described below, in for example, ¶ [0038], before and after propylene glycol monomethyl ether acetate (PGMEA) exposure).

[0014] **Figure 3A** is the cross-section of the material before PGMEA exposure.

[0015] **Figure 3B** is the selective surface of the material before PGMEA exposure.

- [0016] **Figure 3C** is the cross-section of the material after PGMEA exposure.
- [0017] **Figure 3D** is the selective surface of the material after PGMEA exposure.
- [0018] **Figure 4** is an illustration of a method for making the material of the invention
- [0019] **Figure 5A** is an illustration of crosslinking the polymer matrix at a mesoporous region of the material of the invention
- [0020] **Figure 5B** is an illustration of crosslinking the polymer matrix at a macroporous region of the material of the invention
- [0021] **Figure 5C** is an illustration of crosslinking the pore lining polymer region of a mesopore of the material of the invention

SUMMARY OF THE INVENTION

- [0022] The invention relates to hierarchically porous, isoporous crosslinked block copolymer structures, i.e., cross-linked structures, where at least one of the blocks is chemically modified to have chemical resistance properties to harsh solvent conditions from organic, acidic or basic materials, and other blocks provide mechanical integrity to the structure, to enhance their suitability for various environments. The multiblock polymer is chemically modified and crosslinked after the formation of the isoporous multiblock polymer material whereby sites within and along wall surfaces defining pores are crosslinked.
- [0023] The present invention relates to block copolymer structures where at least one of the blocks is chemically crosslinked to impart chemical resistance to harsh solvent conditions from

organic, acidic or basic materials, and other blocks provide mechanical integrity to the structure, to enhance its suitability for various separation environments, after isoporosity is obtained.

[0024] The invention also includes separating an analyte of interest with high permeability and excellent selectivity, the membrane has uniform porosity, by contacting a non-aqueous liquid containing an analyte of interest with the isoporous crosslinked block polymer structures with at least two distinct polymer blocks.

[0025] The invention also includes separating an analyte of interest with high permeability and excellent selectivity from a harsh chemical mixture generated by organic, acidic or basic liquids and the analyte of interest, by contacting the mixture with the isoporous crosslinked block polymer structure.

[0026] The invention also includes a process of maintaining the integrity of an isoporous block polymer structures by chemically modifying at least one of the blocks with a crosslinking reaction after isoporosity is obtained.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The invention is an isoporous structure, e.g., a membrane, film, fabric, monolith which comprises at least one multiblock polymer (MBP) where at least one block of at least one MBP includes at least a portion that is crosslinked. In this context, isoporous means having a substantially narrow pore diameter distribution. The incorporation of crosslinking imparts chemical resistance properties to the isoporous block copolymer (BCP) structure. The crosslinked material may exhibit increased resistance to temperature or harsh media compared to the uncrosslinked material. This

combination of crosslinked polymer blocks in a multiblock copolymer (e.g. A-B, A-B-A, A-B-C, A-B-C-A, A-B-A-B, A-B-C-D, or A-B-C-D-E, etc.) structure, produced by self-assembly, results in a high permeability and high selectivity isoporous structure for separations in non-aqueous liquid media, e.g., organic or harsh liquid media. The material comprises at least two classes of pores: macropores and mesopores, at least one class of which are isoporous. The mesopores may have pore diameters from about 1 nm to 200 nm. The macropores may have pore diameters from about 200 nm to about 100 microns. An isoporous region comprises a pore (void), a pore lining polymer region, and a polymer matrix region.

[0028] Nonlimiting examples of block copolymer architectures, are identified in Table 1. Different letters denote different chemistries, [A], [B], [C], etc. The notation *-co-* indicates a mixture of chemistries in a specific block. The distribution of mixtures of chemistries may be periodic (ordered), random/statistical, or graded within the block. Other “complex” block structures or polymer architectures are also suitable for the invention, provided the materials self-assemble. In this context, a “complex” block structure or polymer architecture signifies more than one monomer, chemistry, configuration, or structure in at least one block, or adjacent to blocks. A combination of different block copolymer starting materials is another such complex architecture.

TABLE 1

[A]-[B]
[A]-[B]-[C]
[A]-[B]-[C-<i>co</i>-D]
[A-<i>co</i>-B]-[C]-[D]

[A-co-B]-[C-co-D]
[A]-[B]-[C]-[D]
[A]-[B]-[C]-[B]-[A]
[A]-[B]-[C]-[D]-[E]

[0029] The crosslinked isoporous structures of the invention are asymmetric, symmetric, partially symmetric, or partially asymmetric.

[0030] The crosslinked structures of the invention are supported by a porous support, or are unsupported. The crosslinked isoporous structure of the invention is the form of two-dimensional (e.g. films, flat sheets) or three-dimensional (e.g. monoliths, beads, hollow fibers, tubular) configuration.

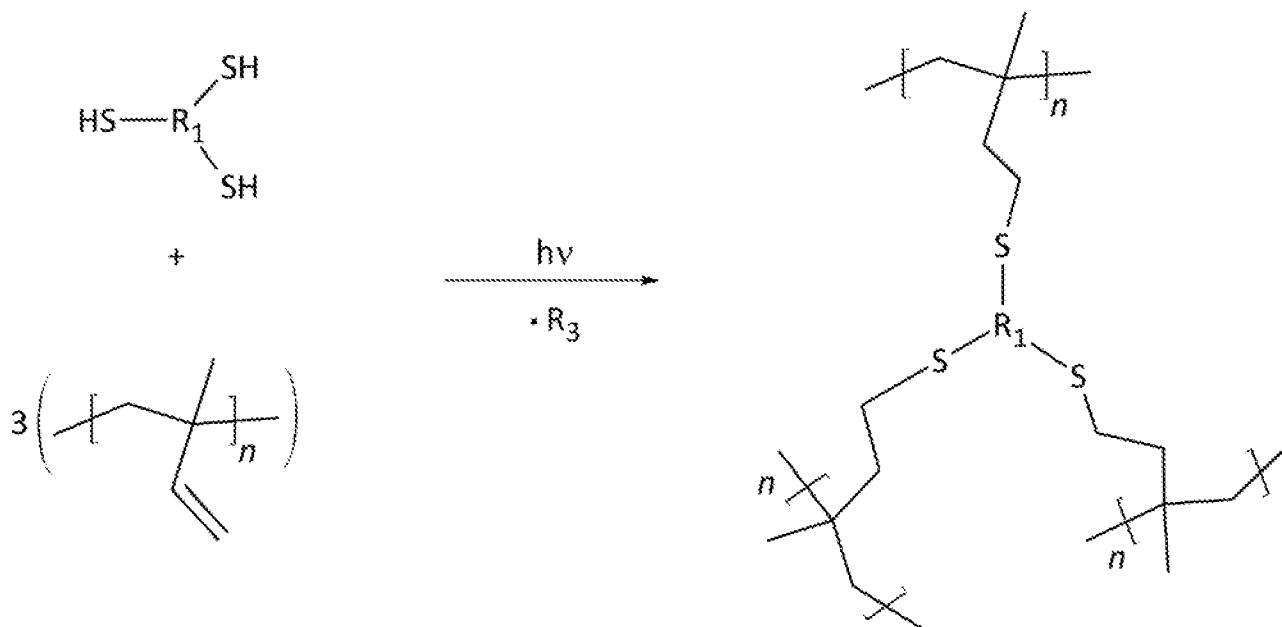
[0031] The crosslinked isoporous structures of the invention are suitable as a separation media, or as a fabric with desirable protective properties (e.g. clothing, bandages) and thus the materials can be used as a separation media, or as a fabric with desirable protective properties. In the liquid-based separation application, the liquids being exposed to the crosslinked isoporous structures of the invention are not limited to purely aqueous solutions. The chemical stability imparted to the crosslinked isoporous structures of the invention from the crosslinking allows solutions contacting the membrane to contain in part, or completely, non-aqueous liquids, as well as aqueous solutions that may otherwise degrade, decompose, or dissolve non-crosslinked structures. The harsh media in which the crosslinked isoporous structures of the invention are used include highly acidic solutions, highly basic solutions, petrochemical products, organic solvents, and other organic small molecules.

The crosslinking of the block copolymers also imparts further heat resistance to the membranes, allowing operation at elevated temperatures.

[0032] The multiblock polymer must at least partially self-assemble when processed from a deposition solution comprising the multiblock polymer and a solvent system. During the process, at least a portion of the solvent system is removed; then, the material is exposed to a phase separation solvent system, such that at least a portion of the polymer material precipitates. Once the pores of the isoporous material are formed, the material is crosslinked through a chemical reaction whereby both material surface cross-linking and interstitial pore cross-linking can occur, which would not occur if cross-linking was conducted prior to pore formation, as illustrated in **Figure 4**. The region of the porous material that is crosslinked is not limited to one region. For example, macroporous regions, or mesoporous regions, or pore lining regions, or any combination thereof may be crosslinked. **Figure 5A** illustrates an embodiment where a mesoporous region is crosslinked. **Figure 5B** illustrates an embodiment where a macroporous region of the material is crosslinked. **Figure 5C** illustrates an embodiment where a pore lining polymer region of a mesopore of the material is crosslinked.

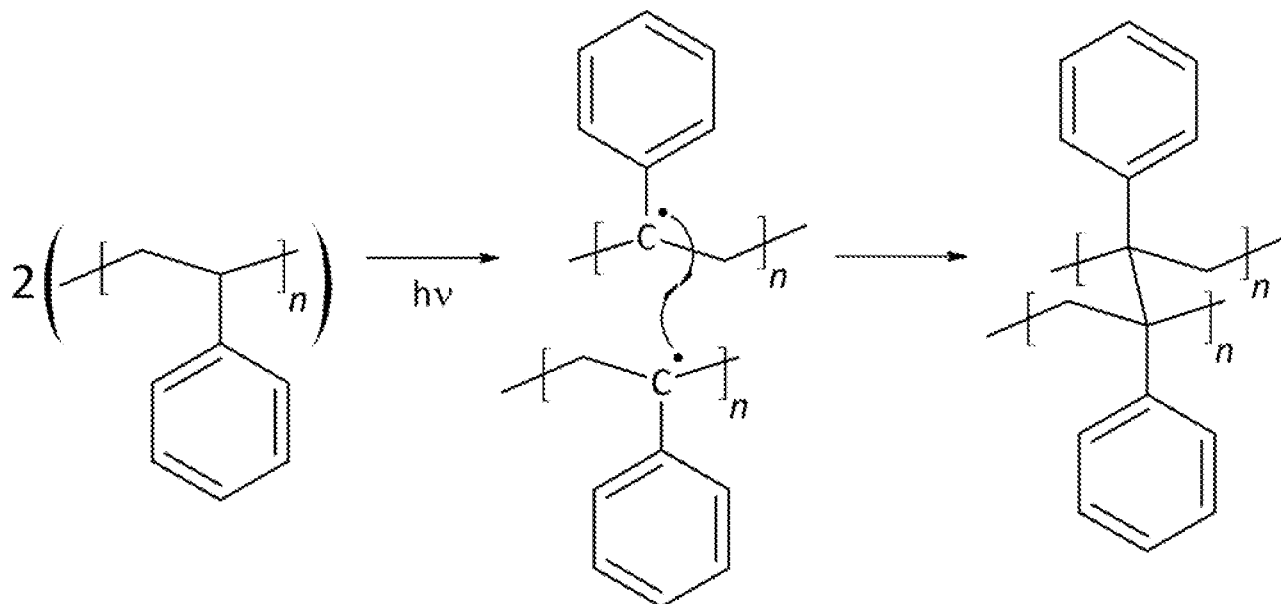
[0033] One approach for achieving the invention is: 1) Dissolution of multiblock polymer and optionally crosslinking agent, in at least one chemical solvent 2) Dispensing polymer solution onto a substrate or mold, or through a die or template 3) Removal of at least a portion of chemical solvent 4) Exposure to a nonsolvent causing precipitation of at least a portion of the polymer 5) Optionally, a wash step 6) Optionally, exposure to a crosslinking agent 7) Crosslinking reaction

[0034] In some embodiments, the crosslinking reaction is a thiol-ene reaction, wherein multiple thiol units of a multifunctional thiol react with multiple -ene (double bond) units. One example of this embodiment is shown below wherein three double bonds on poly(isoprene) units on different polymer chains react with a trifunctional thiol crosslinker, forming crosslinks:

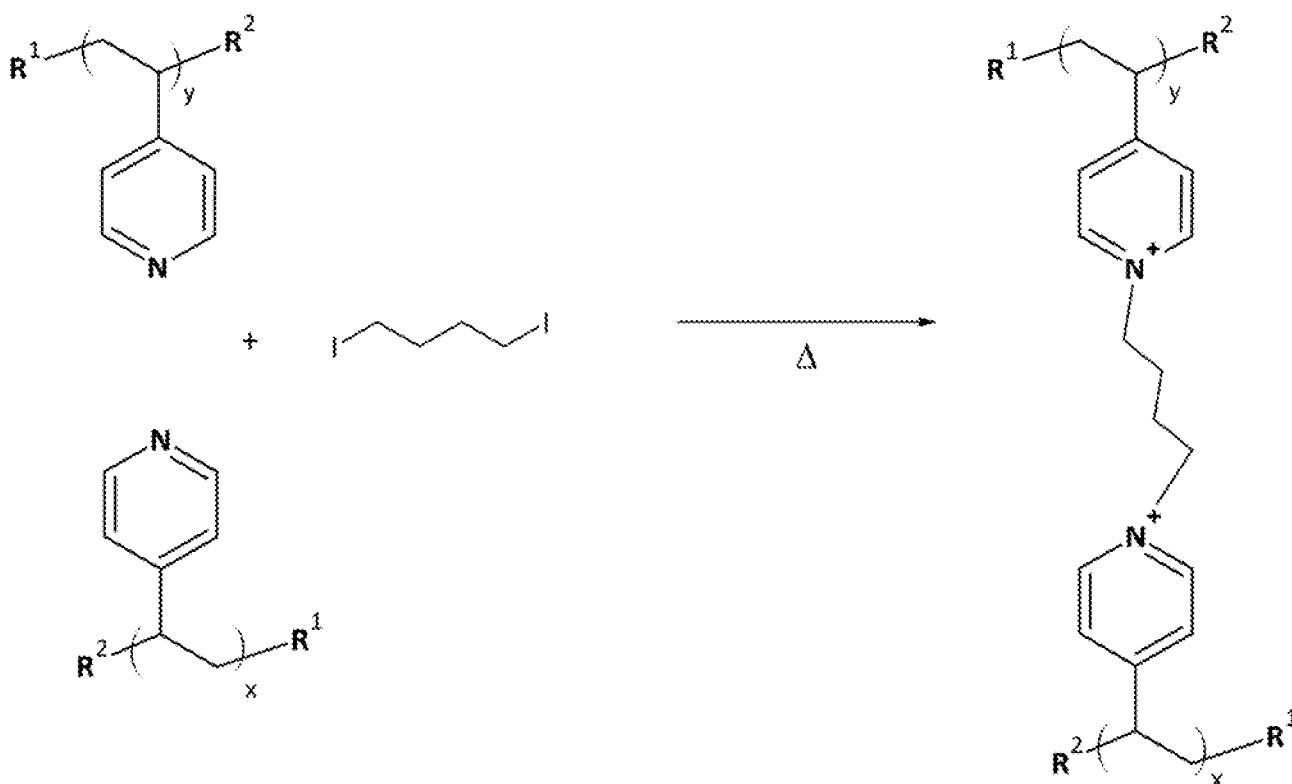


A photoinitiator ($\cdot R^3$) generates radicals with UV irradiation to facilitate the reaction. In one embodiment, a radical generator may be thermally activated to generate radicals

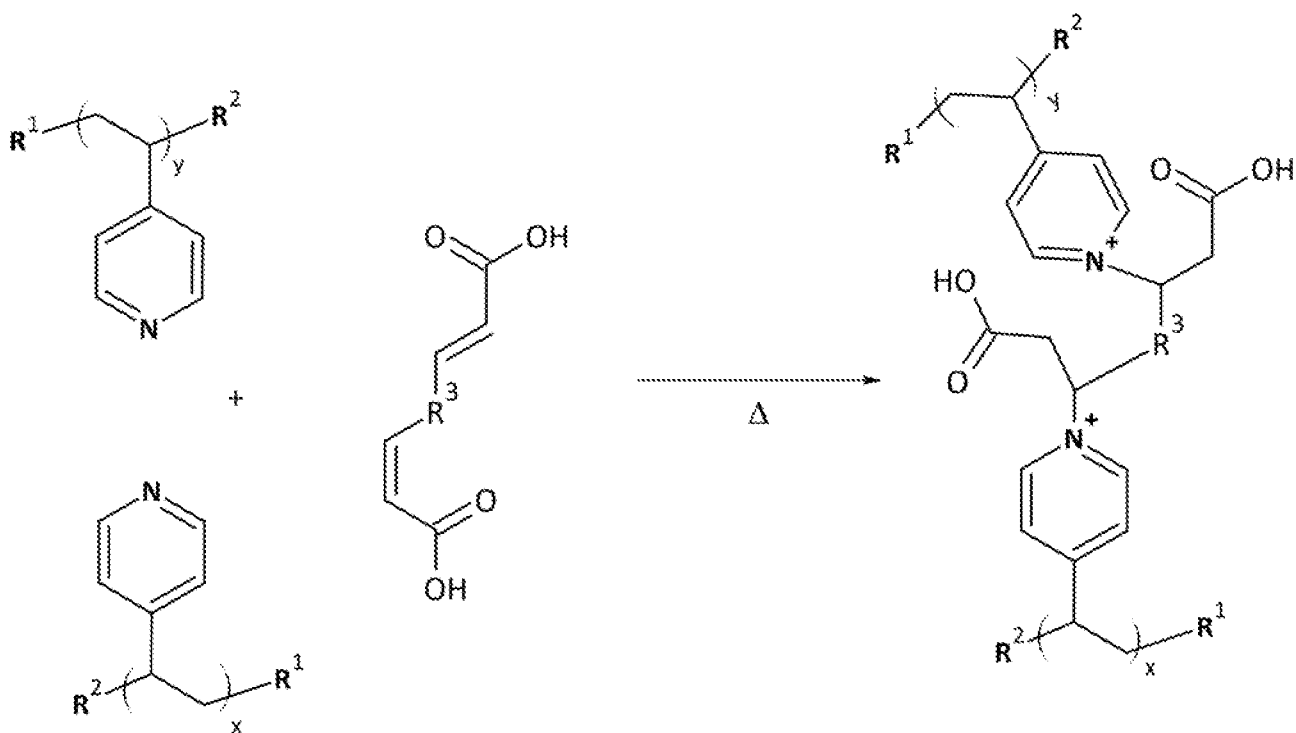
[0035] In some embodiments, the crosslinking reaction is a radical reaction of two polystyrene units reacting to form crosslinks, as shown below:



[0036] In some embodiments, the crosslinking reaction involves a multifunctional crosslinking agent reacting with multiple amine units. In one embodiment, the multifunctional crosslinking agent contains two or more reactive halides selected from bromine, chlorine, and iodine. The halides react with different amine units to generating the crosslinks. An example of this approach is shown below wherein two vinylpyridine units of poly(4-vinylpyridine) on different polymer chains, where R^1 and R^2 represent the adjacent polymer chain sections, and y is equal the number of vinylpyridine monomer units in the 4-vinylpyridine block, react with 1,4-diiodobutane to yield a crosslink:

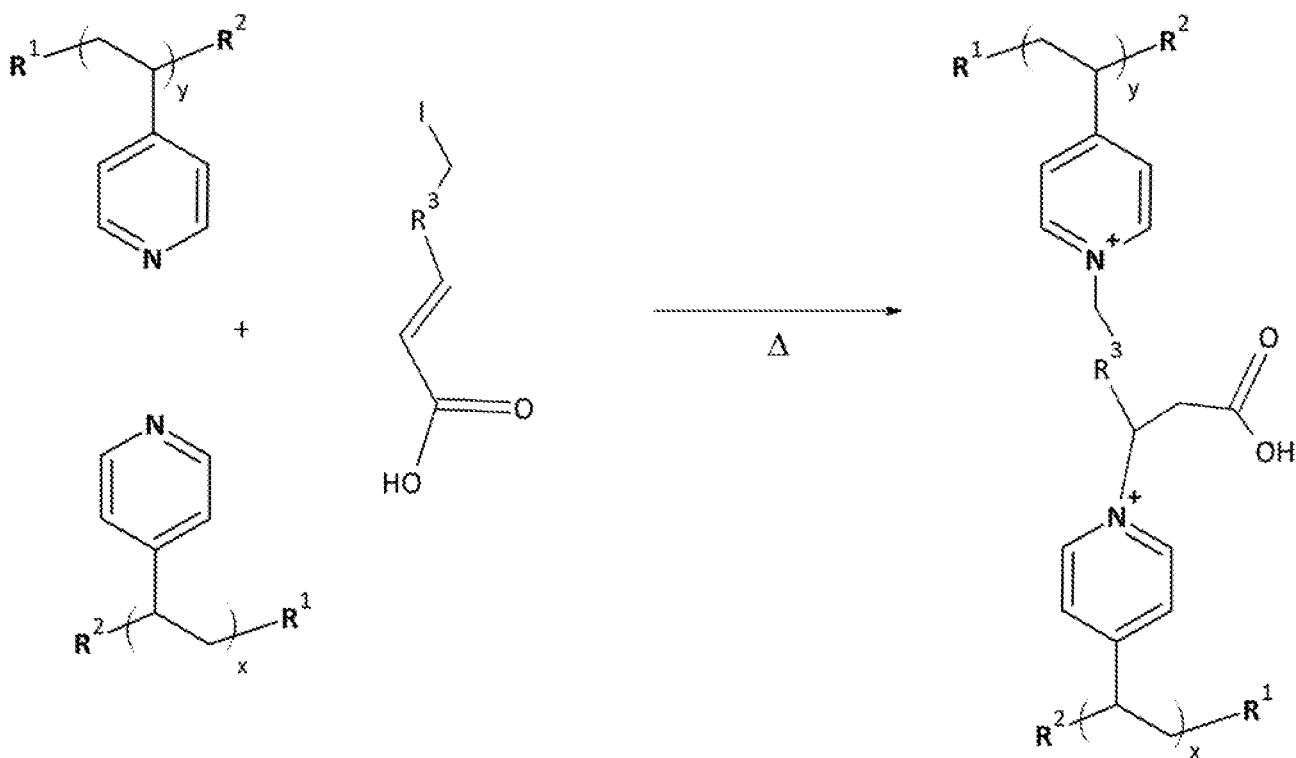


[0037] In another embodiment, the multifunctional crosslinking agent contains two or more reactive double bonds of α,β -unsaturated carbonyl units. The different double bonds undergo Michael addition reactions with amines to generate the crosslinks, where R^1 and R^2 represent the adjacent polymer chain sections, and y is equal the number of vinylpyridine monomer units in the 4-vinylpyridine block, and R^3 is defined as a saturated or unsaturated carbon-containing chain of 1 to 12 carbon atoms as shown below:



[0038] In an embodiment, the multifunctional crosslinking agent contains more than one type of aforementioned crosslinking chemistry (e.g. reactive thiol unit and reactive halide unit, or reactive α,β -unsaturated carbonyl and reactive halide unit). One embodiment where R^1 and R^2 represent the adjacent polymer chain sections, and y is equal the number of vinylpyridine monomer units in the 4-vinylpyridine block, and R^3 is defined as a saturated or unsaturated carbon-containing chain, as

shown below:



In another embodiment, more than one different crosslinking agent is used to crosslink.

[0039] In one embodiment, the block copolymer is the triblock terpolymer poly(isoprene)-*b*-(styrene)-*b*-(4-vinylpyridine) (ISV). The polymer has a volume fraction of about 0.30 poly(isoprene) (PI), 0.55 poly(styrene) (PS), and 0.15 poly(4-vinylpyridine) (P4VP). The polymer is dissolved in a mixture of solvents: 1,4-dioxane and tetrahydrofuran (THF), with a mass ratio of about 7:3 dioxane:THF. A crosslinking agent, pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and photoinitiator, 1-hydroxycyclohexyl phenyl ketone, are added to the polymer solution. The PETMP is about 20% the mass of the polymer, the photoinitiator is about 5% of the mass of the polymer. The solution is processed into a self-assembled asymmetric membrane on a

PET support through the approach in ¶ [0032]. The membrane is crosslinked using the approach in ¶ [0033] through exposure to 254 nm UV irradiation in ambient with a dose of 30 mW/cm² for 5 minutes on each side. After crosslinking, the membranes show increased solvent resistance, as shown in **Figures 1A-1D, 2A-2B, and 3A-3D**. **Figure 1A** shows a scanning electron microscopy (SEM) image of the membrane's cross-section before solvent exposure and **Figure 1C** shows an SEM image of the cross-section after exposure to dimethylformamide (DMF) for 1 minute: the cross-sectional porosity is retained. **Figure 1B** shows an SEM image of the selective surface layer prior to solvent exposure and **Figure 1D** shows an SEM image of the selective surface layer after 1 minute exposure to DMF: the surface porosity is retained, indicating solvent resistance. **Figure 2A** shows an SEM image of the selective surface layer prior to solvent exposure and **Figure 2B** shows an SEM image of the selective surface layer after 1 minute exposure to tetrahydrofuran (THF): the surface porosity is retained, indicating solvent resistance. **Figure 3A** shows a scanning electron microscopy (SEM) image of the membrane's cross-section before solvent exposure and **Figure 3C** shows an SEM image of the cross-section after exposure to propylene glycol monomethyl ether acetate (PGMEA) for 1 minute: the cross-sectional porosity is retained. **Figure 3B** shows an SEM image of the selective surface layer prior to solvent exposure and **Figure 3D** shows an SEM image of the selective surface layer after 1 minute exposure to PGMEA: the surface porosity is retained, indicating solvent resistance. Without crosslinking, the three solvents disrupt the surface porosity and/or dissolve the membranes.

[0040] In some embodiments, the material of the invention is packaged as a device including: a pleated pack, flat sheets in a crossflow cassette, a spiral wound module, hollow fiber, a hollow fiber

module, or as a sensor. In an embodiment, a device utilizes more than one different material of the invention.

[0041] In one embodiment, the material or device comprising the material of the invention has a detectable response to a stimulus/stimuli. For example, the material or device may have a detectable photochemical or electrochemical response to a specific stimulus.

[0042] In some embodiments, the material of the invention, or a device comprising the material of the invention, is used in a process wherein an analyte of interest is separated in a medium containing the analyte of interest contacting the material or device. In one such process, the analyte of interest is separated by binding and eluting. In another such process, solutes or suspended particles are separated by filtered. In another such process, both bind and elute and separation by filtration mechanisms are incorporated.

[0043] In some embodiments, the material of the invention, or a device comprising the material of the invention, is used in a process wherein an analyte of interest is detected in a medium containing the analyte of interest contacting the material or device. In one such process, the analyte of interest is detected by a response of the material/device to the presence of the analyte of interest.

[0044] In some embodiments, more than one different material of the invention is packaged together as a kit. In other embodiments, more than one device comprising the material of the invention is packaged together as a kit. For example, a kit may include multiple materials of the invention; the materials may be the same or different. For example, a kit may include multiple devices comprising the material of the invention; the devices may be the same or different.

[0045] In some embodiments, the material of the invention is immobilized to or integrated with a support or a textile. For example, the materials may be supported on a porous or nonporous support for mechanical integrity. In another example, the material may be integrated with a textile for a garment such as a gas permeable but solvent resistant garment.

[0046] One approach for the fabrication of the invention is post-modifying isoporous block copolymer materials to be crosslinked. This approach involves directly chemically modifying the multiblock polymer.

[0047] The amount of crosslinking and chemistry is controllable. This is controlled through varying the amount of crosslinking reagents or crosslinking conditions e.g. UV dose, temperature, crosslinking agent concentration. One or more different crosslinking chemistries and/or one or more different polymer blocks may be used.

[0048] One variant is partially or completely crosslinking units of more than one block of the constituent copolymer. Which block(s) is/are crosslinked is not limited to the block that comprises the structure's major surface.

[0049] The porous material has a layer having a thickness of from about 5 nm to about 500 nm, in unit (nm) increments and ranges therebetween, and a plurality of mesopores about 1 nm to about 200 nm in diameter, in said layer. In an embodiment, the mesopores are in the range of about 1 nm to about 200 nm. In an embodiment, the mesopores are in the range of about 3 nm to about 200 nm. In an embodiment, the mesopores are in the range of about 5 nm to about 200 nm. In an embodiment, the mesopores are in the range of about 1 nm to about 100 nm. In an embodiment, the mesopores are in the range of about 5 nm to about 100 nm. In an embodiment, the mesopores are in

the range of about 10 nm to about 100 nm. The material may also have a bulk layer having a thickness of from about 2 microns to about 500 microns, including macropores having a size of from about 200 nm to about 100 microns. Isoporous block copolymer membranes incorporating crosslinking in/on at least a portion of at least one block of the block copolymer. This imparts chemical resistance to the membranes. The crosslinked material exhibits increased resistance to temperature or harsh media compared to the uncrosslinked material.

[0050] The pore size of the mesoporous region of the membrane is also controllable.

[0051] The polymers may be synthesized in any manner with the proviso that the polymer can self-assemble and form the porous material through the methods of the invention and at least a portion of at least one block can be subsequently crosslinked.

[0052] Advantages of this invention include: no required thermal annealing for the self-assembly process, no wasted material necessitating removal to form porosity, enables thick material for mechanical stability, enables freestanding material, enables asymmetric structures for increased surface accessibility.

[0053] Table of selected features of Figures 1-5

	Label	Feature
10		Polymer matrix of mesoporous region
20		Pore lining polymer region of mesoporous region
30		Mesopore (void)
40		Polymer matrix of macroporous region
50		Pore lining polymer region of macroporous region
60		Macropore (void)
100		Crosslinked polymer matrix of mesoporous region

110	Crosslinked polymer matrix of macroporous region
120	Crosslinked pore lining polymer region of mesoporous region
130	Crosslinking reaction
140	Polymer solution with or without crosslinker in storage container
145	Storage container
150	Dispensing polymer solution into desired configuration
160	Self-assembling polymer solution
170	Exposure to nonsolvent
180	Nonsolvent molecule
190	Precipitating polymeric material
210	Porous crosslinked polymer material

CLAIMS

1. A self-assembled multiblock crosslinked polymer material comprising at least two polymer chains, wherein each chain has distinct blocks at least one of which is a poly(4-vinylpyridine) and wherein the material self assembles into at least a bulk layer having a thickness of 2 microns to 500 microns and a surface layer having a thickness of 5 nm to 500 nm;
wherein the bulk layer comprises at least macropores having a size of 200 nm to 100 microns;
wherein the surface layer comprises at least mesopores having a size of 1 nm to 200 nm;
wherein at least a portion of one or both of the macropores and mesopores are isoporous;
wherein at least a portion of at least one poly(4-vinylpyridine) block is crosslinked to at least one different poly(4-vinylpyridine) block on at least one of said at least two polymer chains; and
wherein the crosslinking provides chemical resistance and the thickness of the bulk layer provides mechanical integrity to the polymer material upon exposure to solvent conditions selected from the group consisting of acidic solvents, basic solvents, organic solvents, and a combination thereof.
2. The material of claim 1, wherein the material is one of asymmetric or symmetric.
3. The material of claim 1 or 2, wherein the material further comprises a porous support onto which the material is self-assembled.
4. The material of any one of claims 1-3, wherein the at least two polymer chains comprise poly(isoprene)-b- (styrene)-b-(4-vinylpyridine) (ISV).
5. The material of any one of claims 1-4, wherein both the macropores of the bulk layer and the mesopores of the surface layer are crosslinked.
6. The material of any one of claims 1-5, wherein the at least one poly(4-vinylpyridine) block has been crosslinked to the at least one different poly(4-vinylpyridine) block via a multifunctional crosslinking agent reacting with multiple amine units.

7. The material of any one of claims 1-5, wherein the at least one poly(4-vinylpyridine) block has been crosslinked to the at least one different poly(4-vinylpyridine) block via a multifunctional crosslinking agent comprising both a reactive thiol unit and a reactive halide unit or comprising both a reactive α,β -unsaturated carbonyl and a reactive halide unit.

8. The material of any one of claims 1-5, wherein the at least one poly(4-vinylpyridine) block has been crosslinked to the at least one different poly(4-vinylpyridine) block by a saturated or unsaturated carbon-containing chain of 1 to 12 carbon atoms.

9. The material of any one of claims 1-8, wherein the material is used as a separation media, or as a fabric with desirable protective properties.

10. The material of any one of claims 1-8, wherein the crosslinked material exhibits increased resistance to temperature or harsh media compared to the uncrosslinked material.

11. A method of preparing a self-assembled multi block crosslinked polymer material, comprising:

a. forming an isoporous structure with both macropores and mesopores from a multi block copolymer material, wherein the multi block copolymer material comprising at least two polymer chains, wherein each chain has distinct blocks at least one of which is a poly(4-vinylpyridine) wherein the multi block copolymer material self assembles into at least a bulk layer having a thickness of 2 microns to 500 microns and a surface layer having a thickness of 5 nm to 500 nm, wherein the bulk layer comprises at least macropores having a size of 200 nm to 100 microns, wherein the surface layer comprises at least mesopores having a size of 1 nm to 200 nm, and wherein at least a portion of one or both of the macropores and mesopores are isoporous; and

b. crosslinking at least a portion of at least one poly(4-vinylpyridine) block with a chemical reaction;

wherein the crosslinking provides chemical resistance and the thickness of the bulk layer provides mechanical integrity to the polymer material upon exposure to solvent conditions selected from the group consisting of acidic solvents, basic solvents, organic solvents, and a combination thereof.

12. The method of claim 11 wherein the isoporous material is formed by:
- a. dissolution of multi block polymer and optionally crosslinking agent, in at least one chemical solvent
 - b. dispensing polymer solution onto a substrate or mold, or through a die or template
 - c. removal of at least a portion of chemical solvent
 - d. exposure to a nonsolvent causing precipitation of at least a portion of the polymer
 - e. crosslinking reaction.
13. The method of claim 12, wherein the steps to form the isoporous material further comprise:
- d-i. a wash step.
14. The method of claim 12 or 13, wherein the steps to form the isoporous material further comprise:
- d-ii: exposure to a crosslinking agent.
15. The method of any one of claims 11-14, wherein the crosslinking agent comprises a multifunctional crosslinking agent capable of reacting with multiple amine units, optionally a photoinitiator which generates radicals upon UV radiation exposure.
16. The method of any one of claims 11-14, wherein the crosslinking agent comprises a multifunctional crosslinking agent comprising both a reactive thiol unit and a reactive halide unit or comprising both a reactive α,β -unsaturated carbonyl and a reactive halide unit.
17. The method of any one of claims 11-14, wherein the crosslinking agent comprises a multifunctional halide compound with two or more reactive halide groups selected from bromine, chlorine, or iodine, and at least a portion of at least one polymer block comprises a crosslinkable polymer unit comprising at least one reactive amine.
18. The method of any one of claims 11-14, wherein the crosslinking agent comprises a multifunctional α,β -unsaturated carbonyl compound with two or more reactive α,β -unsaturated

carbonyl units, and at least a portion of at least one polymer block comprising a crosslinkable polymer unit comprises at least one reactive amine.

19. The method of any one of claims 11-14, wherein the crosslinking agent comprises a halide and α,β -unsaturated carbonyl compound with two or more reactive groups comprising at least one α,β -unsaturated carbonyl unit and at least one halide, and at least a portion of at least one polymer block comprising a crosslinkable polymer unit comprising at least one reactive amine.

20. The method of any one of claims 11-19, wherein the multiblock copolymer material in step (a) is self assembled onto a porous support.

21. The method of any one of claims 11-20, wherein the multiblock copolymer material comprises poly(isoprene)-b- (styrene)-b-(4-vinylpyridine) (ISV).

22. The method of any one of claims 11-21, wherein the crosslinking in step (b) comprises crosslinking both the macropores of the bulk layer and the mesopores of the surface layer.

23. A process separating or detecting an analyte of interest contacting a medium containing the analyte of interest with a material of any one of claims 1-8.

24. A device comprising the material of any one of claims 1-8.

25. The device of claim 24, wherein the device is selected from a pleated pack, flat sheets in a crossflow cassette, a spiral wound module, hollow fiber, a hollow fiber module, or a sensor.