SULFONATED POLY(ARYLENE ETHER) MEMBRANES WITH HIGH MONOVALENT SALT REJECTION EVEN IN THE PRESENCE OF MIXED SALT FEEDS THAT CONTAIN MULTIVALENT SALTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to U.S. Provisional Application Nos. 62/628,347 and 62/628,349, both filed on February 9, 2018. These applications are hereby incorporated by reference in their entireties.

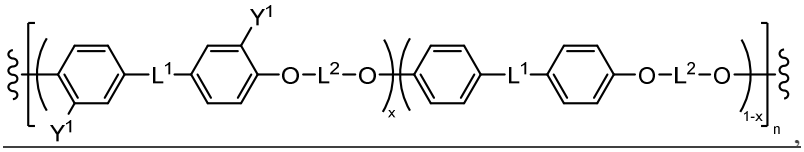
BACKGROUND

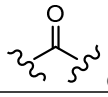
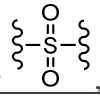
[0002] Clean water is critical to the safety, security and survivability of mankind. Nearly 41% of the Earth's population lives in water-stressed areas, and water scarcity will be exacerbated by an increasing population. According to the U.S. Geological Survey, ~96.5% of the Earth's water is located in seas and oceans with the remaining in surface and ground water, mostly frozen in glaciers and ice caps. Approximately 96% of the total water is saline, and only ~0.8% is considered to be accessible fresh water. Thus, saltwater desalination is important for tackling the problem of water scarcity. Thermal desalination methods are not energetically efficient because they rely on an energy-intensive phase change and require a large quantity of fuel to vaporize the water. Membrane based desalination processes are more economical and energetically efficient than thermal methods for seawater desalination and for other related water purification applications. Anionic sulfonated poly(arylene ether) membranes for water desalination have been shown to have high water permeability and good rejection of monovalent salts (e.g., NaCl), but prior membranes made from such materials are typically not very good at rejecting monovalent ions (e.g., Na^+ Cl^-) in the presence of polyvalent cations (e.g., Ca^{2+}, Mg^{2+}, etc.). Given that polyvalent salts are found in virtually all saline water and surface water sources, further development is needed.

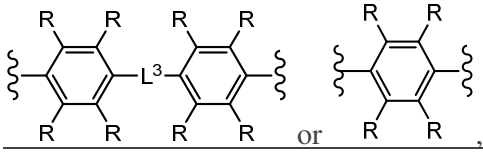
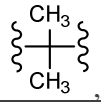
SUMMARY ~~OF THE INVENTION~~

[0003] The present ~~invention~~disclosure relates generally to methods and systems for desalinating water and compositions useful for desalinating water. More particularly, ~~embodiment~~examples of the present ~~invention~~disclosure provide sulfonated poly(arylene ether) polymers, methods of making such polymers, and methods and systems for using such polymers in desalination of water.

[0003a] In one aspect, the present disclosure refers to a copolymer comprising the structure:



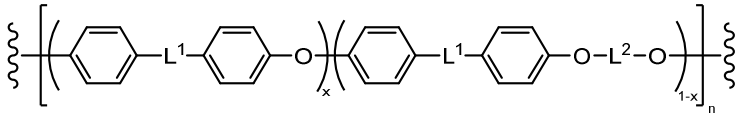
wherein each L^1 is independently  or  , wherein each L^2 is independently

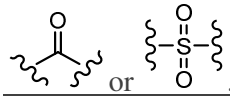
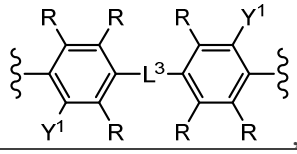
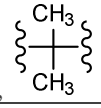
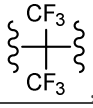
 or , wherein each L^3 is independently a single bond,  , or  , wherein one Y^1 is SO_3Z and the other Y^1 is H, wherein Z is a counterion, and wherein each R is independently H, F, or CH_3;

the value of x is 0 to 1, and the value for n is from 2 to 100,000.

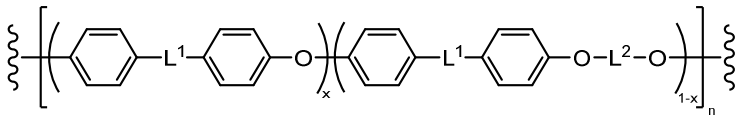
[0003b] In another aspect, the present disclosure refers to a crosslinked network comprising: the copolymer as disclosed herein in crosslinked form; blends of different molecular weights of copolymers as disclosed herein in crosslinked form; or blends of a single molecular weight or different molecular weights of copolymers as disclosed herein and one or more small molecule polymerizable reagents, in crosslinked form.

[0003c] In another aspect, the present disclosure refers to a copolymer comprising the structure:

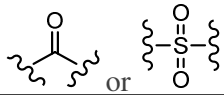
 , where each L^1 is independently

 or , wherein each L^2 is  , wherein each L^3 is independently a single bond,  , or  , wherein at least one or both Y^1 is SO_3Z, wherein Z is a counterion, and wherein each R is independently H, F, or CH_3; the value of x is 0 to 1, and the value for n is from 2 to 100,000.

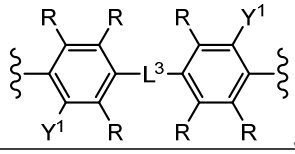
[0003d] In another aspect, the present disclosure refers to a copolymer comprising the structure:



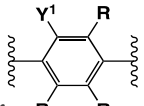
, where each L^1 is independently



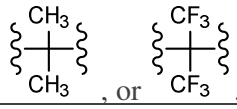
or



, or



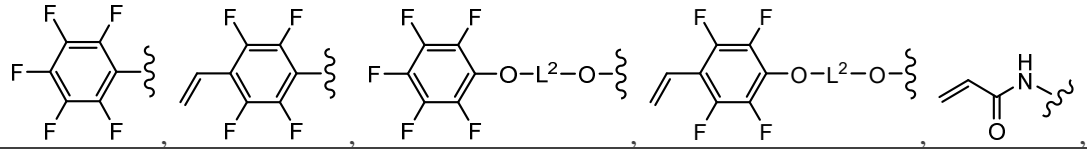
, wherein each L^2 is independently



wherein each L^3 is independently a single bond,

, or

, wherein at least one or all Y^1 is SO_3Z, wherein Z is a counterion, and wherein each R is independently H, F, or CH_3, further comprising one or more terminating groups A, each terminating group A independently selected from H,



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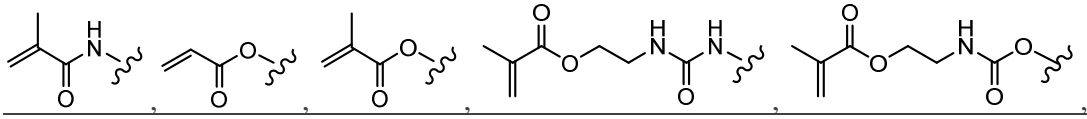


, a phenol, or an aminophenol, the value of x is 0 to 1, and the value for n is from 2 to 100,000.

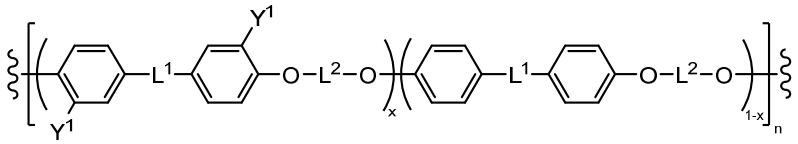
[0003e] In another aspect, the present disclosure refers to a water desalination membrane comprising the copolymer as disclosed herein.

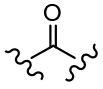
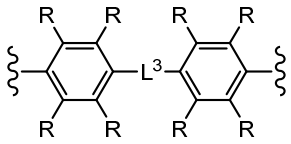
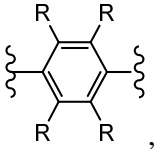
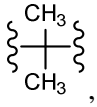
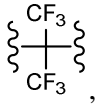
[0003f] In another aspect, the present disclosure refers to a water desalination membrane comprising the crosslinked network as disclosed herein.

[0004] In one ~~aspect~~example, linear sulfonated poly(arylene ether)s are provided. Linear sulfonated polymers may be copolymers, such as polymers comprising two or more different monomer units. The polymers may be polymerized via chemical reaction between monomers. Linear sulfonated

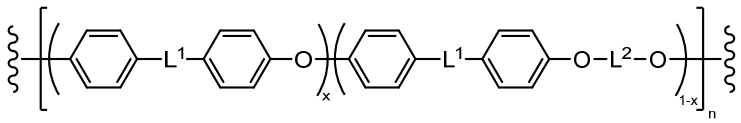
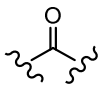
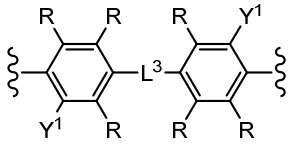
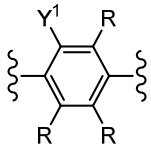
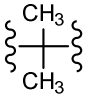
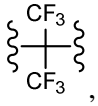
copolymers of this ~~aspect~~example may be formed from presulfonated monomers, meaning that one or more substituents of the monomers may be a sulfonate group (e.g., $-SO_3^-$, SO_3Na, SO_3K, etc.). In some cases, presulfonated and unsulfonated monomers are polymerized to form a copolymer. In other cases, unsulfonated monomers are polymerized to form a copolymer, then sulfonate groups are added in a post-sulfonation reaction.

[0005] In a specific ~~embodiment~~example, a copolymer may comprise the structure:

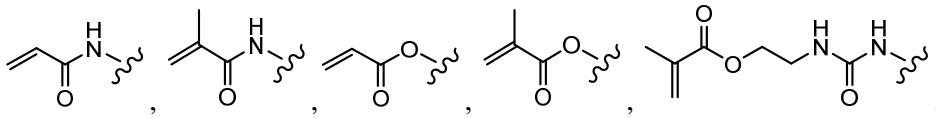
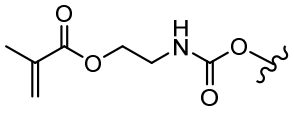


where each L^1 is independently  or  , each L^2 is independently  or  , each L^3 is independently a single bond,  , or  , one Y^1 is SO_3Z and the other Y^1 is H, Z is a counterion (e.g., a metal ion), and each R is independently H, F, or CH_3. Values for x may be from 0 to 1, and values for n may be any suitable number for a polymer, such as from 2 to 100,000, for example.

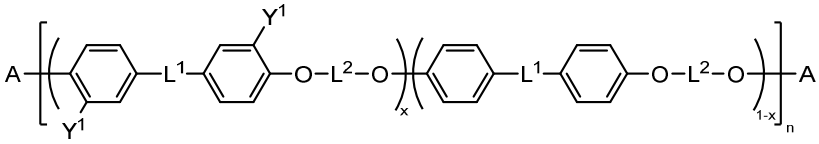
[0006] In another specific ~~embodiment~~example, a copolymer may comprise the structure:

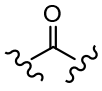
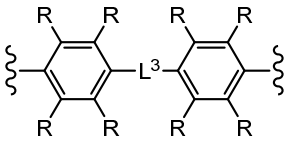
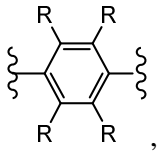
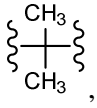
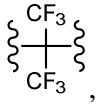
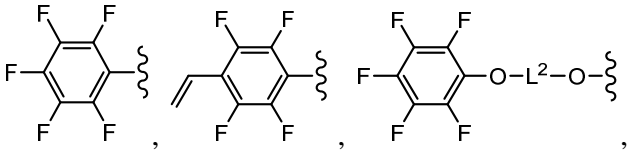
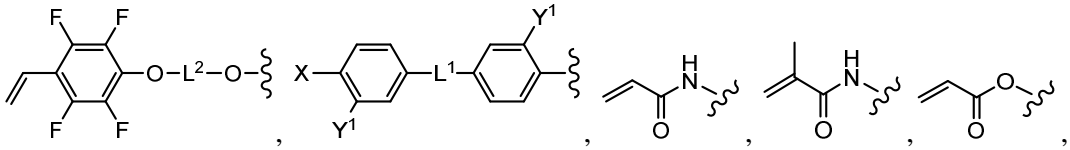
 , where each L^1 is independently  or  , each L^2 is independently  or  , each L^3 is independently a single bond,  , or  , Y^1 is SO_3Z or H, Z is a counterion (e.g., a metal ion), and each R is independently H, F, or CH_3. Values for x may be from 0 to 1, and values for n may be any suitable number for a polymer, such as from 2 to 100,000, for example.

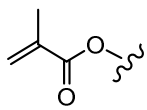
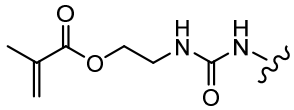
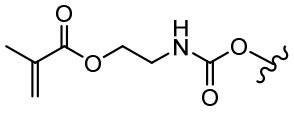
[0007] In some ~~embodiment~~examples, a terminating group on one or both ends of a polymer may be included and the molecular weights may be controlled by adjusting the stoichiometries among the monomers and terminating agents by state of the art methods for synthesizing step-growth copolymers. The terminating groups may include or comprise an alkenyl group, a styrenic group, a

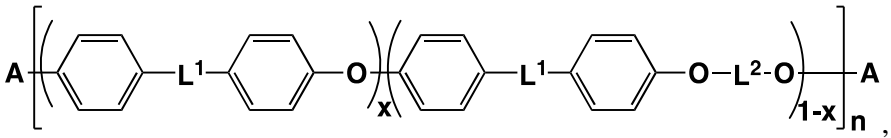
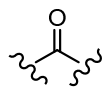
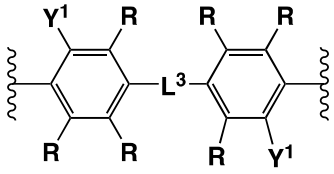
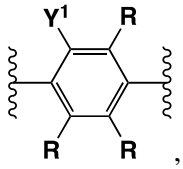
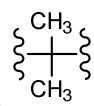
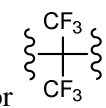
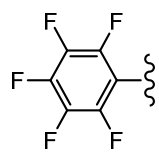
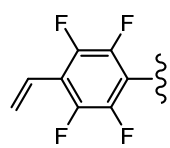
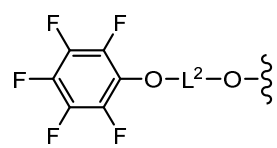
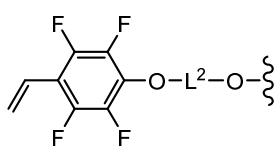
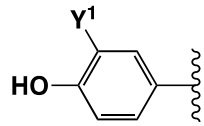
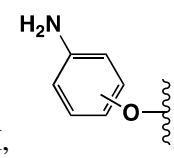
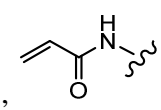
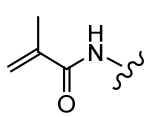
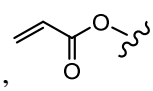
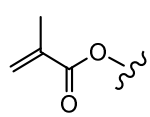
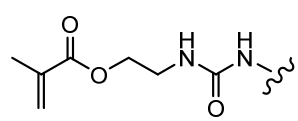
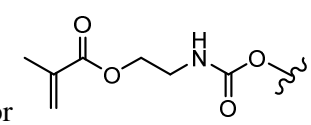
fluorinated styrenic group, a carbonyl group, a carboxylate ester, an amino group, a phenol group, or other crosslinkable groups, which may be useful for permitting crosslinking between polymer chains, such as when exposed to a crosslinking agent. Optionally, a copolymer may comprise or further comprise one or more terminating groups A, each terminating group A independently selected from  ,  , tetrafluorostyrene, an aminophenol or a phenol. By subjecting a copolymer, or a blend of the copolymers with different molecular weights, containing one or more crosslinkable groups to a crosslinking agent, such as heat, light, a free radical initiator, an epoxy reagent, etc., a crosslinked network may be formed of any of the copolymers described herein. Low molecular weight crosslinkable monomers may also be added to these copolymers to make crosslinked networks from such mixtures.

[0008] An example crosslinkable oligomeric macromonomer of this ~~aspect~~example may have the structure:



where each L^1 is independently  or  , each L^2 is independently  or  , each L^3 is independently a single bond,  , or  , each Y^1 is independently H or SO_3Z, Z is a counterion (e.g., Na^+ or K^+), each R is independently H, F, or CH_3, each A is independently,  ,  .

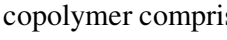
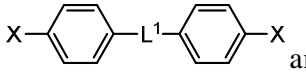
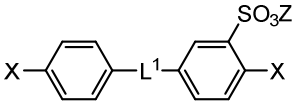
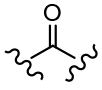
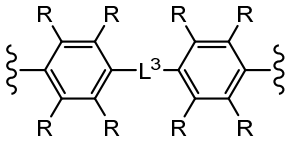
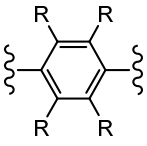
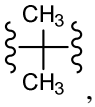
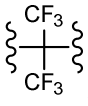
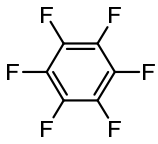
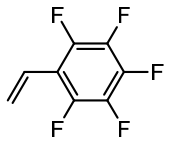
 ,  , or  . **[0009]** Another crosslinkable oligomeric macromonomer prepared by post-sulfonation may have the following structure:

 , where each L^1 is independently  or  , each L^2 is independently  or  , each L^3 is independently a single bond,  , or  , each Y^1 is independently H or SO_3Z, Z is a counterion (e.g., Na^+ or K^+), each R is independently H, F, or CH_3, and each A is independently,  ,  ,  ,  ,  where Y^1 is SO_3Z or H,  ,  ,  ,  ,  ,  , or  .

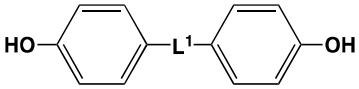
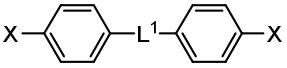
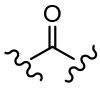
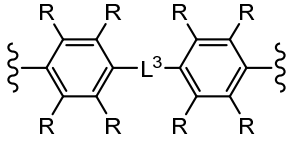
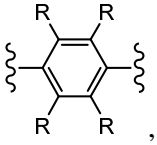
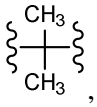
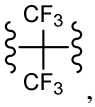
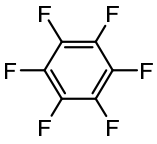
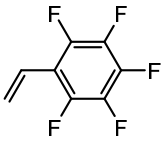
[0010] Functional oligomeric macromonomers of the above ~~aspect~~examples may optionally be crosslinked, such as after exposure to a crosslinking agent. Optionally, blends of functional oligomeric macromonomers with different crosslinkable terminating agents or with different molecular weights may be crosslinked together, or low molecular weight monomers or crosslinking agents may be added to the mixture.

[0011] Copolymers described herein may have any suitable molecular weight or length. The copolymers described herein are generally random copolymers in which a fractional amount (x or 1-x) of a sulfonate containing structural unit ranges from about 5% to about 95%, which may optionally be referred to herein as the degree of sulfonation. Example fractional amounts of

sulfonate containing structural units may include from 5% to 10%, from 10% to 15%, from 15% to 20%, from 20% to 25%, from 25% to 30%, from 30% to 35%, from 35% to 40%, from 40% to 45%, from 45% to 50%, from 50% to 55%, from 55% to 60%, from 60% to 65%, from 65% to 70%, from 70% to 75%, from 75% to 80%, from 80% to 85%, from 85% to 90%, or from 90% to 95%. It will be appreciated that the copolymer molecular weight or length and/or the fractional amounts of sulfonate containing structural units in a copolymer may dictate the copolymer's properties, which may in turn impact the suitability of the polymer for use in different applications. For example, the amount of sulfonation may correlate with the ion exchange capacity (IEC) of the copolymer. Optionally, the IEC may be expressed in units of milliequivalents per gram of dry polymer. Example IEC values for the copolymers described herein may range from about 0.1 to about 5, such as from 0.1 to 0.5, from 0.5 to 1, from 1 to 2, from 2 to 3, from 3 to 4, or from 4 to 5.

[0012] In another ~~aspect~~example, synthetic methods are described herein. In some ~~embodiment~~examples, methods of making copolymers are described. An example method of making a copolymer comprises reacting  with  and  , optionally together with an aminophenol to endcap the copolymer and control the molecular weight, to generate a copolymer, where each L^1 is independently  or  , L^2 is  or  , L^3 is a single bond,  , or  , each R is independently H, F, or CH_3, and X is a halogen. Optionally, a method of this ~~aspect~~example further comprises exposing the copolymer terminated with either a phenol or with an aromatic amine derived from reaction with an aminophenol to a crosslinking agent. Optionally, a method of this ~~aspect~~example further comprises reacting a copolymer having phenol endgroups with  or  , or reacting a copolymer with phenol or aminophenol endgroups with an acryloyl halide (e.g., acryloyl chloride), a methacryloyl halide (e.g., methacryloyl chloride), isocyanatoethyl acrylate or isocyanatoethyl methacrylate to generate an end-functionalized copolymer. Optionally,

the end-functionalized copolymer may be crosslinked by exposure to a crosslinking agent, such as heat, light, a free radical initiator, or an epoxy reagent.

[0013] Another method of making a copolymer comprises reacting $HO-L^2-OH$ with  and  , optionally together with an aminophenol, to generate a copolymer, where each L^1 is independently  or , L^2 is  or  , L^3 is a single bond,  , or  , each R is independently H, F, or CH_3, and X is a halogen. The stoichiometry can be offset to generate controlled molecular weight macromonomers with phenol endgroups by state of the art methods for step-growth polymers, or aminophenol can be added in calculated amounts to generate controlled molecular weight copolymers with aromatic amine endgroups. Then those phenol or aromatic amine terminated macromonomers can be post-sulfonated to generate approximately one SO_3Z group on each ring of L^2, where Z is a counterion. Optionally, methods of this ~~aspect~~example further comprise reacting the phenol terminated copolymer or a sulfonated copolymer with  ,  , or a phenol or aminophenol terminated copolymer or sulfonated copolymer with an acryloyl halide, a methacryloyl halide, isocyanatoethyl acrylate, or isocyanatoethyl methacrylate to generate an end-functionalized copolymer or end-functionalized sulfonated copolymer. Optionally, methods of this ~~aspect~~example further comprise reacting the end-functionalized copolymer with a sulfonating reagent such as sulfuric acid to post-sulfonate the end-functionalized copolymer and generate an end-functionalized sulfonated copolymer. Optionally, methods of this ~~aspect~~example may include a crosslinking step, such as a step comprising initiating a crosslinking reaction by subjecting the end-functional phenol, aromatic amine from aminophenol, fluorostyrene, fluoroinated aromatic, acrylate, acrylamide, methacrylate, methacrylamide, or urea or urethane acrylate or methacrylate terminated copolymer to a crosslinking agent, such as heat, light, a free radical initiator or an epoxy reagent.

[0014] It will be appreciated that each of the aforementioned groups or structures in this summary section may be unsubstituted or substituted, meaning that any hydrogen atom may be replaced by another group as described below.

[0015] In another ~~aspect~~example, water desalination membranes are described. An example desalination membrane may comprise any one or more of the copolymers described herein. Various different properties may be established in the desalination membrane by selection of suitable copolymers. For example, it may be desirable to employ copolymers with crosslinkable endgroups to permit crosslinking in the membrane, such as to provide or increase mechanical robustness in the membrane. Linear sulfonated poly(arylene ether sulfone)s are known to be relatively stable toward aqueous chlorine compounds commonly used as disinfectants in water treatment systems. To retain chlorine stability in the crosslinked networks, it may be desirable to employ copolymers with terminal groups or crosslinking agents that are also stable toward chlorine, e.g., fluorinated endgroups for crosslinking. Advantageously, membranes comprising the polymers and copolymers described herein may be useful for desalinating water including mixed valence salts (e.g., monovalent salts, such as those comprising Na^+ and K^+ with appropriate counterions, and polyvalent salts, such as those comprising Ca^{2+}, Mg^{2+} with appropriate counterions, and any other ionic species). Prior sulfonated desalination membranes may exhibit poor performance for rejecting monovalent ions when divalent cations are present in a feed, but membranes comprising the polymers and copolymers described herein exhibit high rejection of monovalent ions despite the presence of divalent or polyvalent cations in a feed. For example, the water desalination membranes described herein may exhibit a rejection of aqueous monovalent ions of over 90% in the presence of polyvalent cations. Optionally, the rejection may be greater than or about 90%, greater than or about 91%, greater than or about 92%, greater than or about 93%, greater than or about 94%, greater than or about 95%, greater than or about 96%, greater than or about 97%, greater than or about 98%, greater than or about 99%, greater than or about 99.5%, or greater than or about 99.9%.

[0016] In another ~~aspect~~example, methods of desalinating water utilizing the sulfonated poly(arylene ether) membranes of this ~~invention~~disclosure are also described herein, such as with water including mixed salts and combinations of salts with mixed valencies.

[0017] A method of this ~~aspect~~example comprises exposing a first side of a sulfonated poly(arylene ether) water desalination membrane to an aqueous salt solution, the aqueous salt solution comprising a mixture of monovalent ions and polyvalent cations, wherein the water desalination membrane comprises a water desalination membrane that can reject at least 90% of the monovalent salts even in the presence of multivalent salts; pressurizing the aqueous salt solution to drive a reverse osmosis process wherein water from the aqueous salt solution passes from the first side of the water desalination membrane through to a second side of the water desalination membrane and wherein at least 90% of the monovalent ions are rejected from passing through the

water desalination membrane in the presence of the polyvalent cations. Optionally, a concentration of the polyvalent cations is from 1 part per million to 5000 parts per million. For example, a concentration of the polyvalent cations may be at least or about 100 parts per million, at least or about 500 parts per million, at least or about 1000 parts per million, at least or about 1500 parts per million or at least or about 2000 parts per million. Optionally, a concentration of the monovalent cations is from 500 parts per million to 50,000 parts per million. For example, a concentration of the monovalent ions may be at least or about 1000 parts per million, at least or about 5000 parts per million, at least or about 10,000 parts per million, at least or about 15,000 parts per million, or at least or about 20,000 parts per million. Optionally, the water is saline water or seawater.

[0018] As noted above, the polymers and copolymers described herein may be stable in the presence of chlorine and chlorine compounds due to the excellent chemical stabilities of sulfonated and unsulfonated poly(arylene ether)s. Optionally, the aqueous salt solution includes a halide-based sterilization agent and the water desalination membrane remains substantially unoxidized by the halide-based sterilization agent.

[0019] These and other ~~embodiment~~examples of the ~~invention~~disclosure along with many of its advantages and features are described in more detail in conjunction with the text below and attached figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 provides an example synthetic route for polymer synthesis.

[0021] FIG. 2 provides an overview of post-sulfonation of a polymer.

[0022] FIG. 3 provides a schematic illustration of a water desalination process.

[0023] FIG. 4 provides an example of the structure of a common desalination membrane, prepared by interfacially polymerizinpg *m*-phenylene diamine and trimesoyl chloride.

[0024] FIG. 5 provides data showing surface roughness of polymeric membranes. Top: an interfacially polymerized polyamide membrane; Bottom: A sulfonated polysulfone membrane.

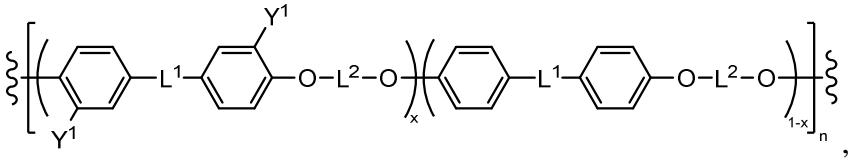
[0025] FIG. 6 provides a schematic illustration of an electrodialysis system.

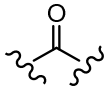
[0026] FIG. 7 provides an overview of an example crosslinking reaction to form an ion exchange membrane.

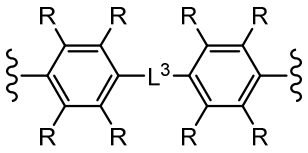
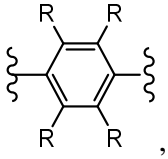
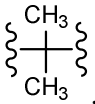
[0027] FIG. 8 provides an overview of an example crosslinking reaction to form a sulfonated poly(arylene ether) network. (5k or 10k block refers to a sulfonated poly(arylene ether) macromonomer)

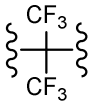
WHAT IS CLAIMED IS:

1. A copolymer comprising the structure:

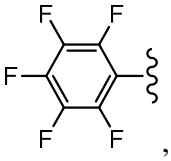
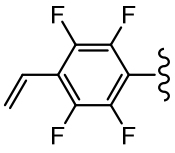


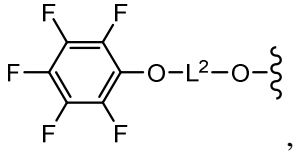
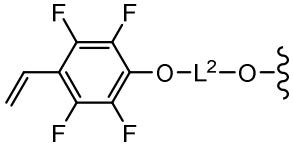
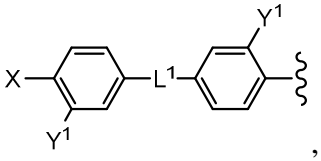
wherein each L^1 is independently  or  , wherein each L^2 is independently

 or  , wherein each L^3 is independently a single bond,  ,

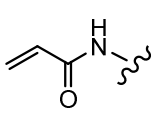
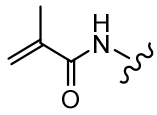
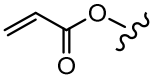
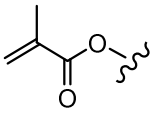
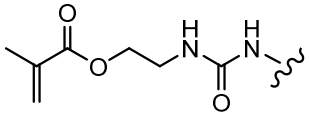
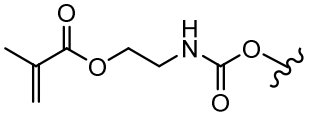
or  , wherein one Y^1 is SO_3Z and the other Y^1 is H, wherein Z is a counterion, and wherein each R is independently H, F, or CH_3; and

the value of x is 0 to 1, and the value for n is from 2 to 100,000.

2. The copolymer of claim 1, further comprising one or more terminating groups A, each terminating group A independently selected from H,  ,  ,

 ,  , a phenol, an aromatic amine derived from an aminophenol as an endcapping agent in the copolymerization, or  ,

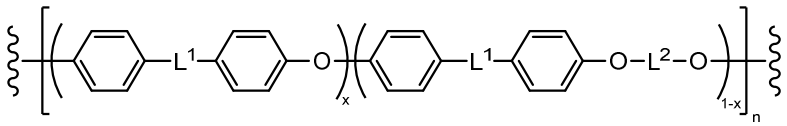
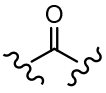
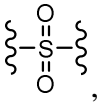
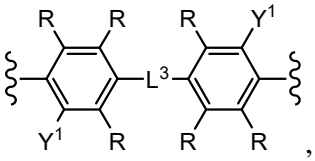
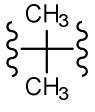
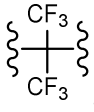
wherein X is a halogen, one Y^1 is SO_3Z and the other Y^1 is H or both Y^1 are H.

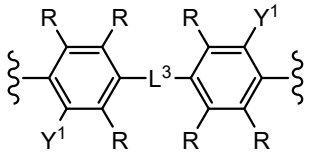
3. The copolymer of claim 1, further comprising one or more terminating groups A, each terminating group A independently selected from  ,  ,  ,  ,  , or  .

4. A crosslinked network comprising:

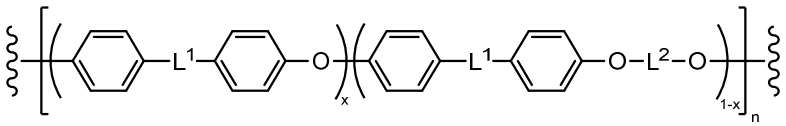
the copolymer of claim 2 or claim 3 in crosslinked form; blends of different molecular weights of copolymers of claim 2 or claim 3 in crosslinked form; or blends of a single molecular weight or different molecular weights of copolymers of claim 2 or claim 3 and one or more small molecule polymerizable reagents, in crosslinked form.

5. A copolymer comprising the structure:

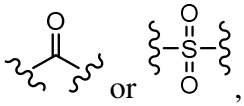
 , where each L^1 is independently  or  , wherein each L^2 is  , wherein each L^3 is independently a single bond,  , or  , wherein at least one or both Y^1 is SO_3Z, wherein Z is a counterion, and wherein each R is independently H, F, or CH_3; the value of x is 0 to 1, and the value for n is from 2 to 100,000.

6. The copolymer of claim 5, wherein each L^2 is  wherein L^3 is a single bond, wherein at least one or both Y^1 is SO_3Z, wherein Z is a counterion, and wherein each R is H or CH_3.

7. A copolymer comprising the structure:

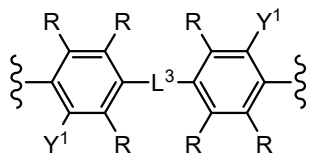


, where each L^1 is independently

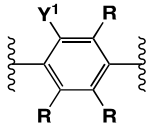


or

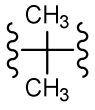
, wherein each L^2 is independently



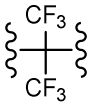
, or



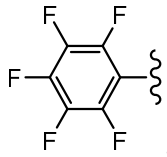
wherein each L^3 is independently a single bond,



, or



, wherein at least one or all Y^1 is SO_3Z, wherein Z is a counterion, and wherein each R is independently H, F, or CH_3, further comprising one or more terminating groups A, each terminating group A independently selected from H,



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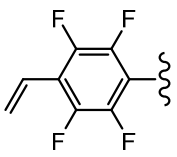

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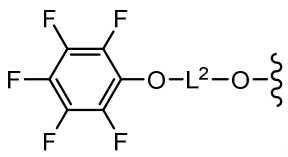

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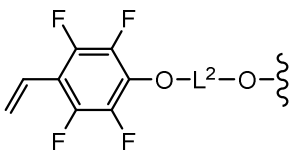

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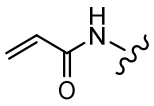

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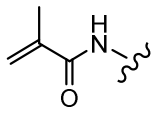

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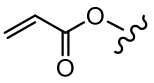

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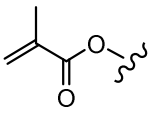

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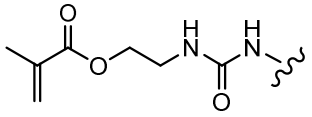

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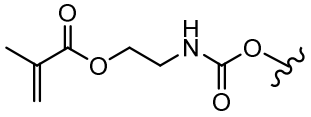
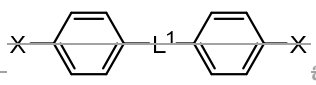


, a phenol, or an aminophenol, the value of x is 0 to 1, and the value for n is from 2 to 100,000.

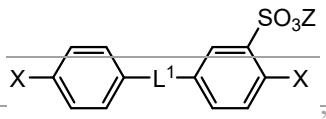
8. A crosslinked network comprising: the copolymer of claim 7 in crosslinked form; blends of different molecular weights of copolymers of claim 7 in crosslinked form; or blends of a single molecular weight or different molecular weights of copolymers of claim 7 and one or more small molecule polymerizable reagents, in crosslinked form.

~~9. A method comprising:~~

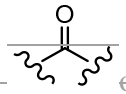
~~reacting $HO{-}L^2{-}OH$ with~~



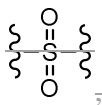
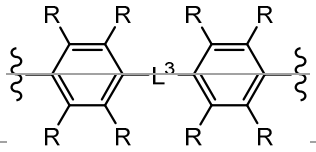
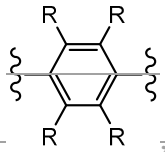
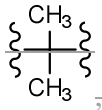
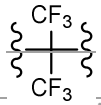
~~and~~



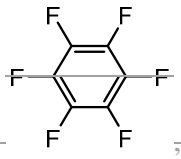
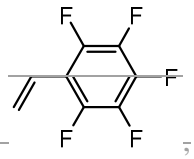
~~, with or without an aminophenol, to generate a copolymer, wherein each L^1 is independently~~



~~or~~


, wherein L^2 is  or  , wherein L^3 is a single bond,  , or  , wherein each R is independently H, F, or CH_3, and wherein X is a halogen.

10. The method of claim 9, further comprising:

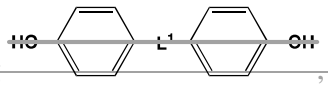
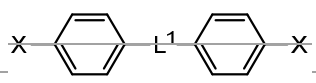
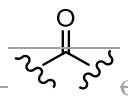
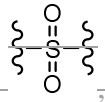
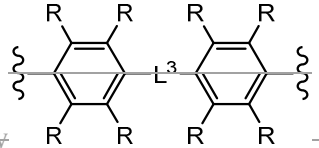
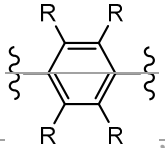
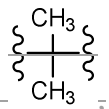


reacting a phenol or aminophenol terminated copolymer with , ; acryloyl halide, methacryloyl halide, isocyanatoethyl acrylate, or isocyanatoethyl methacrylate to generate an end-functionalized copolymer.

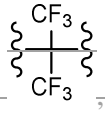
11. The method of claim 9 or 10, further comprising:

initiating a crosslinking reaction by exposing the end-functionalized copolymer to a crosslinking agent including one or more of heat, light, a free radical initiator, or an epoxy reagent.

12. The method of claim 11, wherein the crosslinking reaction includes: crosslinking a blend of different molecular weights of the end-functionalized copolymer; or crosslinking a single molecular weight or blends of different molecular weights of the end-functionalized copolymer and one or more polymerizable reagents.

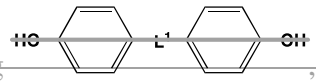
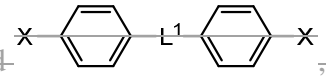
13. A method comprising:

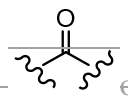
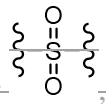
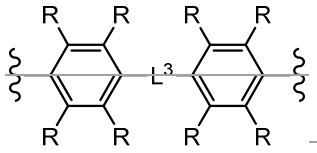
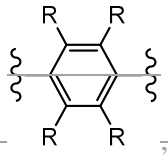
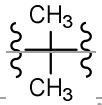
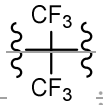
reacting  , one or more $HO-L^2-OH$ and  to generate a copolymer, wherein each L^1 is independently  or  , wherein L^2 is independently  and/or  , wherein L^3 is a single bond,  ,



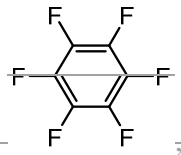
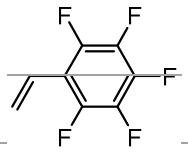
or , and wherein each R is independently H, F, or CH_3; and sulfonating the copolymer to generate a single SO_3Z substituent on one or every aromatic ring of L^2, wherein Z is a counterion.

14. A method comprising:

reacting  , one or more $HO-L^2-OH$ and  ;

with or without an aminophenol, to generate a copolymer with phenol or aminophenol endgroups, wherein each L^1 is independently  or  , wherein L^2 is independently  and/or  , wherein L^3 is a single bond,  , or  ; and

sulfonating the copolymer to generate a single SO_3Z substituent on one or every aromatic ring of L^2, wherein Z is a counterion; and

conducting an end-functionalization reaction with  ,  , acryloyl halide , methacryloyl halide, isocyanatoethyl acrylate, or isocyanatoethyl methacrylate to generate a post-sulfonated, end-functionalized copolymer.

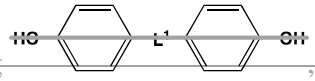
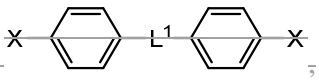
15. The method of claim 14, wherein the end-functionalization reaction is with the copolymer or a post-sulfonated copolymer, or wherein the sulfonation reaction is with the copolymer or the end-functionalized copolymer.

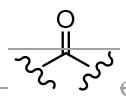
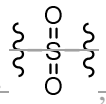
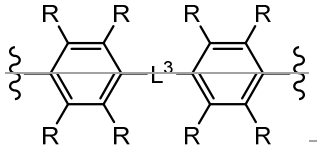
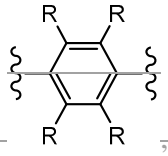
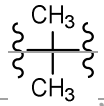
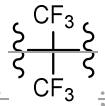
16. The method of any one of claims 13-15, further comprising:

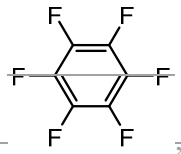
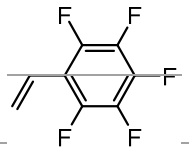
initiating a crosslinking reaction by subjecting the end-functionalized copolymer to a crosslinking agent including one or more of heat, light, a free radical initiator, or an epoxy reagent.

~~17. The method of claim 16, wherein the crosslinking reaction includes: crosslinking a blend of different molecular weights of the end-functionalized copolymer; or crosslinking a single molecular weight or blends of different molecular weights of the end-functionalized copolymer and one or more polymerizable reagents.~~

~~18. A method comprising:~~

~~reacting~~  ~~, one or more~~  ~~and~~  ~~,~~

~~with or without an aminophenol, to generate a copolymer with phenol or aminophenol endgroups, wherein each L^1 is independently~~  ~~or~~  ~~, wherein L^2 is independently~~  ~~and/or~~  ~~, wherein L^3 is a single bond,~~  ~~, or~~  ~~; and~~

 ~~,~~  ~~, acryloyl halide, methacryloyl halide, isocyanatoethyl acrylate, or isocyanatoethyl methacrylate to generate a post-sulfonated, end-functionalized copolymer;~~

~~initiating a crosslinking reaction by subjecting the end-functionalized copolymer to a crosslinking agent including one or more of heat, light, a free radical initiator, or an epoxy reagent. wherein the crosslinking reaction includes: crosslinking a blend of different molecular weights of the end-functionalized copolymer; or crosslinking a single molecular weight or blends of different molecular weights of the end-functionalized copolymer and one or more polymerizable reagents; and~~

~~sulfonating the crosslinked copolymer to generate a single SO_3Z substituent on some, one, or every aromatic ring of L^2, wherein Z is a counterion.~~

~~19~~ 9. A water desalination membrane comprising the copolymer of any one of claims 1-3 or 5-7.

~~20~~ 10. The water desalination membrane of claim ~~19~~ 9 exhibiting a rejection of aqueous monovalent ions of over 95% in the presence of polyvalent cations.

~~21~~ 11. A water desalination membrane comprising the crosslinked network of claim 4.

~~22~~ 12. The water desalination membrane of claim ~~21~~ 11 exhibiting a rejection of aqueous monovalent ions of over 95% in the presence of polyvalent cations.

~~23~~ 13. A water desalination membrane comprising the crosslinked network of claim 8.

~~24~~ 14. The water desalination membrane of claim ~~23~~ 13 exhibiting a rejection of aqueous monovalent ions of over 95% in the presence of polyvalent cations.

~~25. A method comprising:~~

~~exposing a first side of a water desalination membrane to an aqueous salt solution, the aqueous salt solution comprising a mixture of monovalent cations and polyvalent cations, wherein the water desalination membrane comprises the water desalination membrane of claim 19; and~~

~~pressurizing the aqueous salt solution to drive a reverse osmosis process wherein water from the aqueous salt solution passes from the first side of the water desalination membrane through to a second side of the water desalination membrane and wherein at least 95% of the monovalent ions are rejected from passing through the water desalination membrane in the presence of the polyvalent cations.~~

~~26. The method of claim 25, wherein the water desalination membrane comprises the water desalination membrane of any one of claims 20-24.~~

~~27. The method of claim 25 or claim 26, wherein a concentration of the polyvalent cations is at least 100 parts per million, wherein a concentration of the monovalent cations is at least 100 parts per million.~~

~~28. The method of claim 25 and 26, wherein the aqueous salt solution includes a chlorine-based sterilization agent and wherein the water desalination membrane remains substantially unoxidized by the chlorine-based sterilization agent.~~