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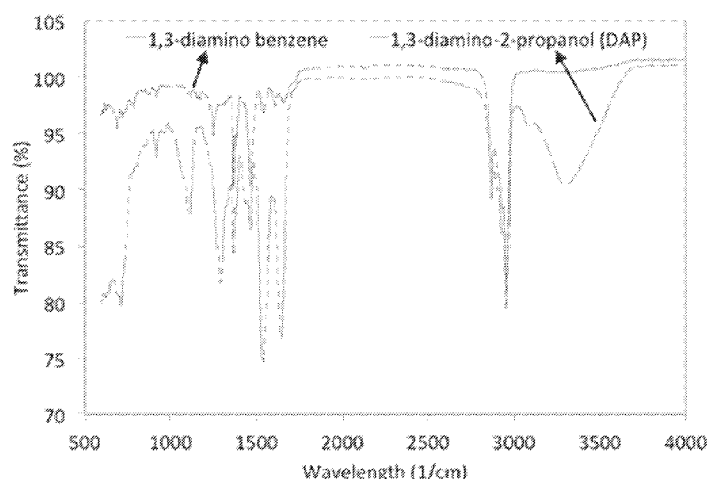


FIG. 1

(57) Abstract: In one aspect, the invention relates to chlorine-tolerant membranes and methods related thereto. The membrane comprises a thin film produced from a reaction by the reaction of a polyfunctional acyl halide and a polyamine. This abstract is intended as a scanning tool for purposes of searching in the particular art and is not intended to be limiting of the present invention.

**CHLORINE-TOLERANT POLYAMIDE DERIVATIVES FOR PREPARING
BIOFOULING-RESISTANT REVERSE OSMOSIS MEMBRANES AND MEMBRANES
MADE THEREFROM**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims the benefit of U.S. Provisional Application No. 61/748,431, filed on January 2, 2013, which is incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with Government support under Grant No. NSF DGE-0903720, awarded by the National Science Foundation. The Government has certain rights in this invention.

BACKGROUND

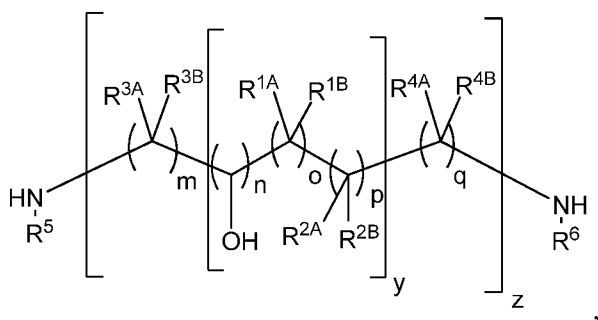
[0003] Membranes used in filtration, such as reverse osmosis (RO) filtration, should be stable (i.e. not degrade) so that the membrane can be used for an extended period of time while maintaining its performance. Commercially available seawater RO membranes, such as meta-phenylenediamine (MPD), have a tendency to degrade in chlorine rich environments. Thus, a MPD membrane can only be used for short periods of time in chlorine rich environments before its performance is impaired due to the degradation of the membrane. Thus, there is a need for a membrane that is stable in chlorine rich environments.

[0004] Despite advances in the understanding of polyamide-coated membranes, degradation due to chlorination sensitivity remains a serious challenge. Thus, there remains a need for chlorine-tolerant polyamide membranes. Such membranes and methods related thereto are described herein.

SUMMARY

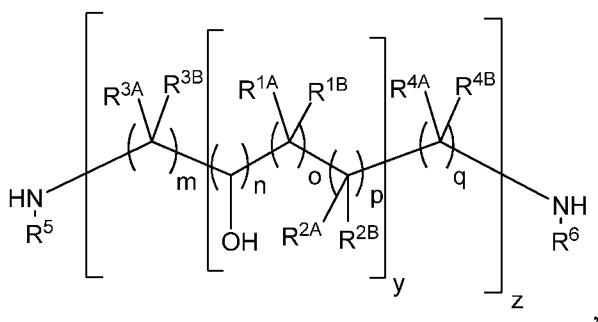
[0005] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, the invention, in one aspect, relates to chlorine-tolerant polyamide membranes and their uses.

[0006] Disclosed is a chlorine-tolerant membranes comprising: a) a porous support membrane; b) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure:



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$; wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6.

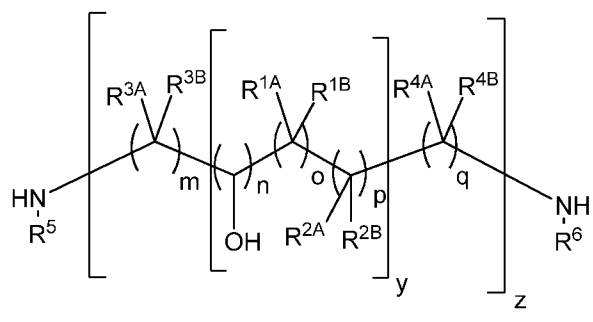
[0007] Also disclosed is a chlorine-tolerant membranes comprising: a) a porous support membrane; b) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure:



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$; wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6; and c) a coating of a second film on the thin film, wherein the second film comprises crosslinked polyvinyl alcohol film.

[0008] Also disclosed herein is a method of purifying water comprising filtering water through a membrane disclosed herein.

[0009] Also disclosed herein is a method of producing the methods disclosed herein, the method comprises the steps of: a) providing, on the surface of a porous support membrane, a composition comprising: i) a polyamine having the structure:



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$; wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6; ii) a polyfunctional acyl halide; (b) polymerizing the polyamine and the polyfunctional acyl halide on the surface of the porous support membrane, thereby producing a thin film; and c) a coating of a second film on the thin film, wherein the second film comprises crosslinked polyvinyl alcohol film.

[0010] While aspects of the present invention can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of skill in the art will understand that each aspect of the present invention can be described and claimed in any statutory class. Unless otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its

steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is in no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

BRIEF DESCRIPTION OF THE FIGURES

[0011] The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention.

[0012] FIG. 1 shows representative data pertaining to the incorporation of DAP and MPD in interfacially polymerized thin films.

[0013] FIG. 2 shows representative data pertaining to the relative change in water and salt permeability for MPD- and DAP-based composite membranes.

[0014] FIG. 3 show representative data pertaining to the surface topography of as-cast MPD-TMC (3A) and DAP-TMC membranes (3B).

[0015] Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DETAILED DESCRIPTION

[0016] The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

[0017] Before the present compounds, compositions, articles, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic

methods unless otherwise specified, or to particular reagents unless otherwise specified, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0018] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The publications discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein may be different from the actual publication dates, which can require independent confirmation.

A. DEFINITIONS

[0019] As used herein, nomenclature for compounds, including organic compounds, can be given using common names, IUPAC, IUBMB, or CAS recommendations for nomenclature. When one or more stereochemical features are present, Cahn-Ingold-Prelog rules for stereochemistry can be employed to designate stereochemical priority, *E/Z* specification, and the like. One of skill in the art can readily ascertain the structure of a compound if given a name, either by systemic reduction of the compound structure using naming conventions, or by commercially available software, such as CHEMDRAWTM (Cambridgesoft Corporation, U.S.A.).

[0020] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a component,” “a polymer,” or “a particle” includes mixtures of two or more such components, polymers, or particles, and the like.

[0021] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the

particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that when a value is disclosed that “less than or equal to” the value, “greater than or equal to the value” and possible ranges between values are also disclosed, as appropriately understood by the skilled artisan. For example, if the value “10” is disclosed the “less than or equal to 10” as well as “greater than or equal to 10” is also disclosed. It is also understood that throughout the application, data is provided in a number of different formats and that this data represents endpoints and starting points, and ranges for any combination of the data points. For example, if a particular data point “10” and a particular data point 15 are disclosed, it is understood that greater than, greater than or equal to, less than, less than or equal to, and equal to 10 and 15 are considered disclosed as well as between 10 and 15. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0022] References in the specification and concluding claims to parts by weight of a particular element or component in a composition denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0023] A weight percent (wt. %) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0024] As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0025] As used herein, the terms “effective amount” and “amount effective” refer to an amount that is sufficient to achieve the desired result or to have an effect on an undesired condition.

[0026] The term “stable”, as used herein, refers to compositions that are not substantially altered when subjected to conditions to allow for their production, detection, and, in certain aspects, their recovery, purification, and use for one or more of the purposes disclosed herein.

[0027] As used herein, the term “polymer” refers to a relatively high molecular weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit, the monomer (e.g., polyethylene, rubber, cellulose). Synthetic polymers are typically formed by addition or condensation polymerization of monomers.

[0028] As used herein, the term “homopolymer” refers to a polymer formed from a single type of repeating unit (monomer residue).

[0029] As used herein, the term “copolymer” refers to a polymer formed from two or more different repeating units (monomer residues). By way of example and without limitation, a copolymer can be an alternating copolymer, a random copolymer, a block copolymer, or a graft copolymer. It is also contemplated that, in certain aspects, various block segments of a block copolymer can themselves comprise copolymers.

[0030] As used herein, the term “oligomer” refers to a relatively low molecular weight polymer in which the number of repeating units is between two and ten, for example, from two to eight, from two to six, or from two to four. In one aspect, a collection of oligomers can have an average number of repeating units of from about two to about ten, for example, from about two to about eight, from about two to about six, or from about two to about four.

[0031] As used herein, the term “cross-linked polymer” refers to a polymer having bonds linking one polymer chain to another.

[0032] The term “alkyl” as used herein is a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *s*-butyl, *t*-butyl, *n*-pentyl, isopentyl, *s*-pentyl, neopentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can be cyclic or acyclic. The alkyl group can be branched or unbranched. The alkyl group can

also be substituted or unsubstituted. For example, the alkyl group can be substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, amino, ether, halide, hydroxy, nitro, silyl, sulfo-oxo, or thiol, as described herein. A “lower alkyl” group is an alkyl group containing from one to six (e.g., from one to four) carbon atoms. Non-limiting examples of alkyls include C1-18 alkyl, C1-C12 alkyl, C1-C8 alkyl, C1-C6 alkyl, C1-C3 alkyl, and C1 alkyl.

[0033] Throughout the specification “alkyl” is generally used to refer to both unsubstituted alkyl groups and substituted alkyl groups; however, substituted alkyl groups are also specifically referred to herein by identifying the specific substituent(s) on the alkyl group. For example, the term “halogenated alkyl” or “haloalkyl” specifically refers to an alkyl group that is substituted with one or more halide, *e.g.*, fluorine, chlorine, bromine, or iodine. The term “alkoxyalkyl” specifically refers to an alkyl group that is substituted with one or more alkoxy groups, as described below. The term “alkylamino” specifically refers to an alkyl group that is substituted with one or more amino groups, as described below, and the like. When “alkyl” is used in one instance and a specific term such as “alkylalcohol” is used in another, it is not meant to imply that the term “alkyl” does not also refer to specific terms such as “alkylalcohol” and the like.

[0034] The term “alkenyl” as used herein is a hydrocarbon group of 2 to 24 carbon atoms with a structural formula containing at least one carbon-carbon double bond. The alkenyl group can be unsubstituted or substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol, as described herein. Non-limiting examples of alkenyls include C2-18 alkenyl, C2-12 alkenyl, C2-8 alkenyl, C2-6 alkenyl, and C2-3 alkenyl.

[0035] The term “alkynyl” as used herein is a hydrocarbon group of 2 to 24 carbon atoms with a structural formula containing at least one carbon-carbon triple bond. The alkynyl group can be unsubstituted or substituted with one or more groups including, but not limited to, alkyl, cycloalkyl, alkoxy, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, heteroaryl, aldehyde, amino, carboxylic acid, ester, ether, halide, hydroxy, ketone, azide, nitro, silyl, sulfo-oxo, or thiol, as described herein. Non-limiting examples of alkynyls include C2-18 alkynyl, C2-12 alkynyl, C2-8 alkynyl, C2-6 alkynyl, and C2-3 alkynyl.

[0036] The terms “amine” or “amino” as used herein are represented by the formula $\text{—NA}^1\text{A}^2$, where A^1 and A^2 can be, independently, hydrogen or alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein.

[0037] The term “ester” as used herein is represented by the formula —OC(O)A^1 or —C(O)OA^1 , where A^1 can be alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group as described herein. The term “polyester” as used herein is represented by the formula $\text{—(A}^1\text{O(O)C—A}^2\text{—C(O)O)}_a\text{—}$ or $\text{—(A}^1\text{O(O)C—A}^2\text{—OC(O))}_a\text{—}$, where A^1 and A^2 can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein and “a” is an integer from 1 to 500. “Polyester” is used to describe a group that is produced by the reaction between a compound having at least two carboxylic acid groups with a compound having at least two hydroxyl groups.

[0038] The term “ether” as used herein is represented by the formula A^1OA^2 , where A^1 and A^2 can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein. The term “polyether” as used herein is represented by the formula $\text{—(A}^1\text{O—A}^2\text{O)}_a\text{—}$, where A^1 and A^2 can be, independently, an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl, aryl, or heteroaryl group described herein and “a” is an integer of from 1 to 500. Examples of polyether groups include polyethylene oxide, polypropylene oxide, and polybutylene oxide.

[0039] The term “azide” as used herein is represented by the formula —N_3 .

[0040] The term “thiol” as used herein is represented by the formula —SH .

[0041] Compounds described herein can contain one or more double bonds and, thus, potentially give rise to cis/trans (E/Z) isomers, as well as other conformational isomers. Unless stated to the contrary, the invention includes all such possible isomers, as well as mixtures of such isomers.

[0042] Certain materials, compounds, compositions, and components disclosed herein can be obtained commercially or readily synthesized using techniques generally known to those of skill in the art. For example, the starting materials and reagents used in preparing the disclosed compounds and compositions are either available from commercial suppliers such as Aldrich Chemical Co., (Milwaukee, Wis.), Acros Organics (Morris Plains, N.J.), Fisher Scientific (Pittsburgh, Pa.), or Sigma (St. Louis, Mo.) or are prepared by methods known to those skilled in the art following procedures set forth in references such as Fieser and Fieser’s Reagents for Organic Synthesis, Volumes 1-17 (John Wiley and Sons, 1991);

Rodd's Chemistry of Carbon Compounds, Volumes 1-5 and Supplemental volumes (Elsevier Science Publishers, 1989); Organic Reactions, Volumes 1-40 (John Wiley and Sons, 1991); March's Advanced Organic Chemistry, (John Wiley and Sons, 4th Edition); and Larock's Comprehensive Organic Transformations (VCH Publishers Inc., 1989).

[0043] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; and the number or type of embodiments described in the specification.

[0044] Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds may not be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps

can be performed with any specific aspect or combination of aspects of the methods of the invention.

[0045] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

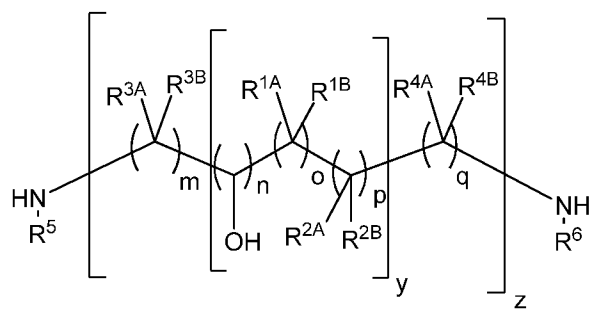
B. CHLORINE-TOLERANT MEMBRANES

[0046] In recent years, reverse osmosis (RO) and nanofiltration (NF) membrane-based desalination and water reuse systems have been built around the world. The technologies are now well accepted, reliable, and cost-effective. However, membrane fouling remains a significant operational and economic driver (Herzberg and Elimelech (2007) *J. Membr. Sci.* **295**: 11-20; Flemming, H. C., et al. (1997) *Desalin* **113**: 215-225; Chen, K. L., Song, L., Ong, S. L., Ng, W. J. (2004) *J. Membr. Sci.* **232**: 63-72). The two most problematic types of fouling are bacterial biofilm formation (“biofouling”) and mineral scale formation (“scaling”). In nearly all NF/RO membrane installations, biofouling drives capital and operating costs through the need for extensive pre-treatment, frequent chemical cleanings, degraded membrane useful life and increased operating pressure; in low-pressure NF/RO applications, scaling drives capital and operating costs by limiting the achievable product water recovery, increasing system size, and requiring use of acid and anti-scalant chemicals. While scaling is largely governed by solubility limits of sparingly soluble minerals (i.e., thermodynamics), biofouling is really only a problem because the most popular modern polyamide composite NF/RO membranes are not chlorine tolerant. However, the high flux of polyamide composite membranes makes them the industry choice. Significant research effort has been expended to produce more fouling-resistant membranes materials, but to date none have proved effective in practical applications (Goosen, M. F. A., et al. (2005) *Sep. Sci. Technol.* **39**: 2261-2297). The development of chlorine tolerant RO membranes could help reduce the cost of membrane-based desalination and advanced water purification by eliminating concerns over biofouling. This will greatly reduce pre-treatment requirements in many applications and results in lower energy consumption, operating costs and capital costs of RO installations.

[0047] Many studies have investigated the chlorine sensitivity of polyamide-coated membranes. The available literature has been reviewed in order to identify the mechanism for degradation of the polyamides upon exposure to chlorine (Glater, J. et al. (1994) *Desalin* **95**: 325-245). Two mechanisms were proposed: direct aromatic substitution and Orton rearrangement. Orton rearrangement involves the adsorption of chlorine onto the amide nitrogen, followed by the transfer of the chlorine to the aromatic ring. Orton rearrangement was experimentally confirmed using model compounds by Kawaguchi and Tamura (Kawaguchi and Tamura (1984) *J. App. Poly. Sci.* **29**: 3359-3367). The same authors also investigated a series of alkyl and aromatic polyamide compounds for chlorine uptake recording a result of no reaction, reversible adsorption, and irreversible adsorption. While tertiary amides showed virtually no uptake of chlorine and aliphatic nitrogen compounds were easily de-chlorinated, secondary amides adjacent to aromatic rings were the most likely to be irreversibly chlorinated. Upon irreversible chlorination, it is suggested that there is a conversion of intermolecular hydrogen bonding between secondary amides and carbonyl groups of adjacent polymer chains into intramolecular hydrogen bonding between the amides and the aromatically linked chlorine of the same chain (Glater, J. et al. (1994) *Desalin* **95**: 325-245). This hydrogen bond conversion results in less dense packing of the polyamide film, thereby compromising salt rejection by the membrane. In addition to hydrogen bond disruption, de-polymerization and cleaving of the polyamide chain itself is also proposed as a possible degradation mechanism.

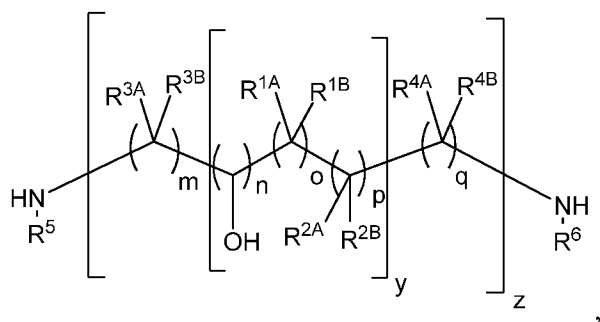
[0048] The problems associated with the membranes disclosed in the art are solved by the membranes disclosed herein.

[0049] In one aspect, the invention relates to chlorine-tolerant membranes comprising: a) a porous support membrane; b) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure:



wherein each of $\text{R}^{1\text{A}}$ and $\text{R}^{1\text{B}}$ is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein $\text{R}^{1\text{A}}$ and $\text{R}^{1\text{B}}$ together is $\text{C}=\text{O}$; wherein each of $\text{R}^{2\text{A}}$ and $\text{R}^{2\text{B}}$ is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein $\text{R}^{2\text{A}}$ and $\text{R}^{2\text{B}}$ together is $\text{C}=\text{O}$; wherein each of $\text{R}^{3\text{A}}$ and $\text{R}^{3\text{B}}$ is independently selected from hydrogen, alkyl, or $-\text{CH}_2\text{OH}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of $\text{R}^{4\text{A}}$ and $\text{R}^{4\text{B}}$ is independently selected from hydrogen, alkyl, and $-\text{CH}_2\text{OH}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-\text{alkyl-hydroxyl}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-\text{alkyl-hydroxyl}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6.

[0050] In one aspect, the invention relates to chlorine-tolerant membranes comprising: a) a porous support membrane; b) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure:



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$; wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6; and c) a coating of a second film on the thin film, wherein the second film comprises crosslinked polyvinyl alcohol film.

[0051] The disclosed chlorine-tolerant polymer membranes allow the chlorination and re-chlorination steps of liquid purification to be eliminated, significantly reducing the complexities of these processes and improving the longevity of the membranes. The resulting process reduces the cost of producing pure water for commercial, agricultural, livestock, and human consumption applications.

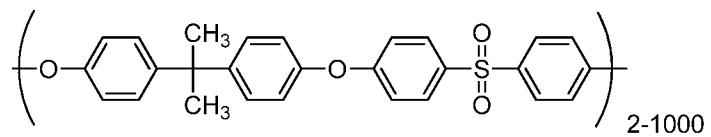
[0052] It is understood that the disclosed compositions, mixtures, and membranes can be employed in connection with the disclosed methods and uses.

1. POROUS SUPPORT MEMBRANE

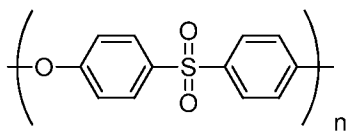
[0053] The chlorine-tolerant water-filtration membranes described herein can comprise a porous support membrane. In various aspects, a semi-permeable polymer film can be polymerized on the porous support membrane. In various aspects, the porous support membrane can comprise a polymer selected from polysulfone, polyethersulfone, polyaniline, or a combination thereof.

[0054] In another aspect, porous support membrane can comprise polyacrylonitrile, polypropylene, cellulose acetate, cellulose diacetate, or cellulose triacetate.

[0055] In various aspects, the porous support membrane can comprise a polysulfone (PSu) support membrane. Any polysulfone membrane known in the art can be utilized as a support membrane in the chlorine-tolerant water-filtration membranes described herein. For example, without wishing to be bound by theory, the polysulfone support membrane can be a commercially available polysulfone ultrafiltration (UF) support membrane. In a further aspect, the polysulfone support membrane can be synthesized by methods known in the art. The structure of polysulfone is:



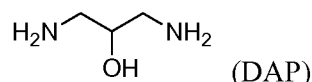
[0056] In various aspects, the porous support membrane can comprise a polyethersulfone (PES) support membrane. In a further aspect, the porous support membrane can comprise polysulfone and polyethersulfone. The structure of polyether sulfone is:



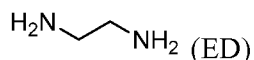
2. THIN FILM

[0057] In order to form thin films of polyamides typical of membrane coating films, diamines are reacted with acyl halides, forming a highly cross-linked polyamide network upon a polymer support membrane such as polysulfone. The diamine is typically dissolved in water while the acyl chloride is dissolved in an organic solvent. The solvent must be immiscible with water in order to form a polymer film only at the surface of the support membrane.

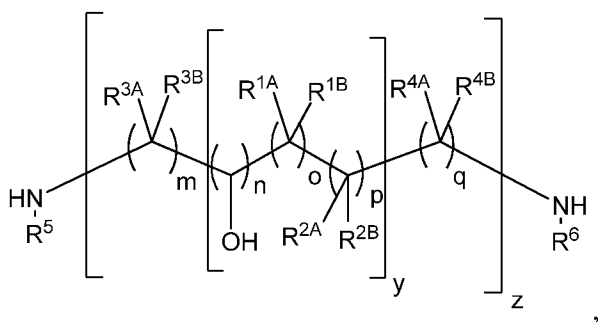
[0058] The thin film excludes the amidic nitrogen adjacent to the aromatic ring, such structure can improve the chlorine resistance of the thin film. Diamine 1,3-diamino-2-propanol (DAP) is an aliphatic molecule that contains a hydroxyl group which endows the molecule with hydrophilic characteristics.



[0059] Hydrophilicity of the thin film is essential for achieving elevated water fluxes and improved bio-fouling resistance. A similar molecule to DAP, 1,2-ethylenediamine (ED), was researched as a diamine during the early years of RO membrane development (Petersen, R. J. (1993) *J. Membr. Sci.* **83**: 81-150). Researchers later discovered, however, that although the formed coating film had fairly high rejection of salts, the hydraulic permeability was prohibitively low. The relatively more hydrophilic nature of DAP has improved performance relative to ED.



[0060] In one aspect, the chlorine-tolerant water-filtration membranes described herein can comprise a thin film. The thin film can be produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure:



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$; wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6.

[0061] Polyfunctional acyl halides are known to those skilled in the art. For example, polyfunctional acyl halides are described in, U.S. Pat. No. 4,277,344, which is incorporated herein by reference. For example, In one aspect, the polyfunctional acyl halide is trimesoyl chloride (TMC).

a. R¹ GROUPS

[0062] In one aspect, each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or R^{1A} and R^{1B} together are C=O.

[0063] In one aspect, R^{1A} and R^{1B} are hydrogen. In another aspect, R^{1A} and R^{1B} are substituted with 0 groups. In yet another aspect, R^{1A} is hydrogen and R^{1B} is selected from alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio.

b. R² GROUPS

[0064] In one aspect, each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or R^{2A} and R^{2B} together are C=O.

[0065] In one aspect, R^{2A} and R^{2B} are hydrogen. In another aspect, R^{2A} and R^{2B} are substituted with 0 groups. In yet another aspect, R^{2A} is hydrogen and R^{2B} is selected from alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio.

c. R³ GROUPS

[0066] In one aspect, each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, and -CH₂OH, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio.

[0067] In one aspect, R^{3A} and R^{3B} are hydrogen. In another aspect, R^{3A} and R^{3B} are substituted with 0 groups. In yet another aspect, R^{3A} is hydrogen and R^{3B} is selected from alkyl, and -CH₂OH.

d. R⁴ GROUPS

[0068] In one aspect, each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and -CH₂OH, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio.

[0069] In one aspect, R^{4A} and R^{4B} are hydrogen. In another aspect, R^{4A} and R^{4B} are substituted with 0 groups. In yet another aspect, R^{4A} is hydrogen and R^{4B} is selected from alkyl, and $-CH_2OH$.

e. R^5 AND R^6 GROUPS

[0070] In one aspect, R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio.

[0071] In one aspect, R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio.

[0072] In one aspect, R^5 and R^6 is hydrogen. In another aspect, R^5 is $alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, and R^6 is hydrogen. For example, R^5 is $alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, and R^6 is hydrogen, and n is 0.

f. m, n, o, p, q, y, and z INTEGERS

[0073] In one aspect, m is an integer from 1-6. For example, m can be 1. In another example, m can be 2, 3, 4, 5, or 6.

[0074] In one aspect, n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen. In one aspect, n is 0. In another aspect, n is 1. In one example, q can be 2, 3, 4, 5, or 6.

[0075] In one aspect, o is an integer from 0-6. For example, o can be 0. In another example, o can be 1. In yet another example, o can be 2, 3, 4, 5, or 6.

[0076] In one aspect, p is an integer from 0-6. For example, p can be 0. In another example, p can be 1. In yet another example, p can be 2, 3, 4, 5, or 6.

[0077] In one aspect, q is an integer from 1-6. For example, q can be 1. In another example, q can be 2, 3, 4, 5, or 6.

[0078] In one aspect, y is an integer from 1-6. For example, y can be 1. In another example, y can be 2, 3, 4, 5, or 6.

[0079] In one aspect, z is an integer from 1-6. For example, z can be 1. In another example, z can be 2, 3, 4, 5, or 6.

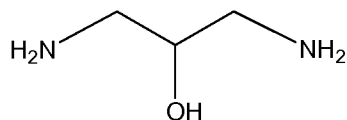
[0080] In one aspect, y and z are 1. In another aspect, n , y and z are 1, and o and p are 0. In yet another example, m is 1, n is 1, o is 1, p is 1, q is 1, y is 1, and z is 1.

[0081] In one aspect, R^{1A} and R^{1B} are hydrogen, R^5 is hydrogen, R^6 is hydrogen, m is 1, n is 1, o is 1, p is 1, q is 1, y is 1, and z is 1. Such compounds are described and produced in U.S. Published application 2011/0152574, which is hereby incorporated by reference in its entirety.

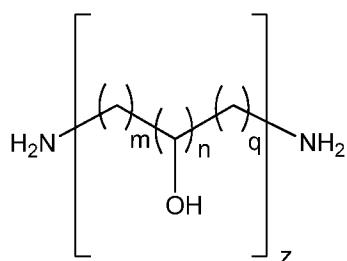
[0082] In one aspect, at least one of R^{1A} , R^{1B} , R^{2A} , or R^{2B} is not hydrogen. In another aspect, at least one of R^{1A} , R^{1B} , R^{2A} , or R^{2B} is amino.

[0083] In another aspect, R^{3A} and R^{3B} are hydrogen, R^{4A} and R^{4B} are hydrogen, R^5 is hydrogen, R^6 is -alkyl-hydroxyl and is substituted with 0 groups, m is 1, n is 0, o is 0, p is 0, q is 1, y is 1, and z is 1.

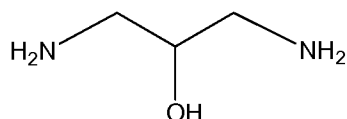
[0084] In one aspect, the polyamine is not



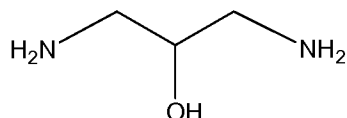
[0085] In another aspect, the polyamine has the structure:



[0086] In one aspect, when a second film is coated on the thin film, the polyamine is



[0087] In one aspect, when a second film is coated on the thin film, the polyamine is not

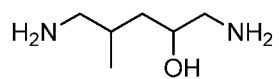
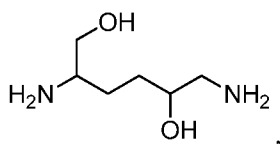
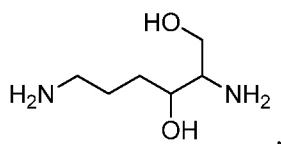
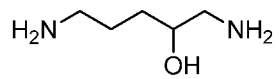
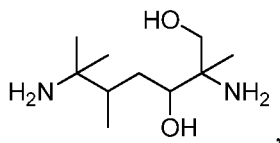
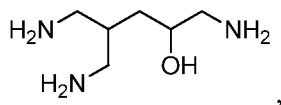
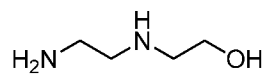
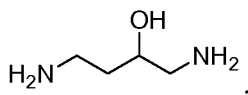
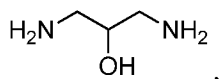


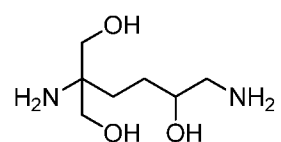
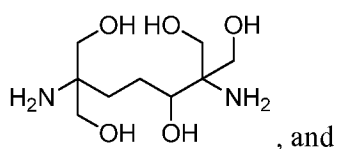
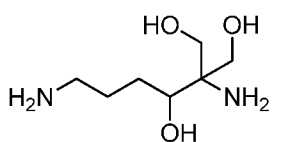
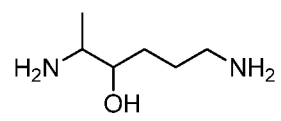
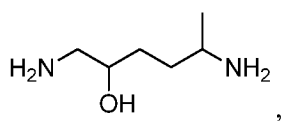
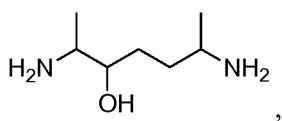
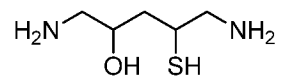
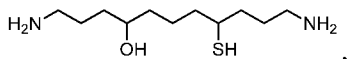
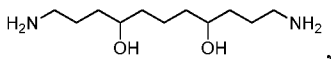
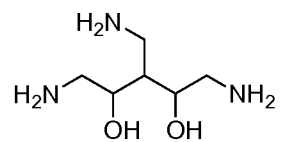
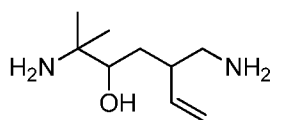
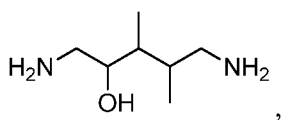
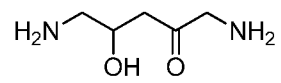
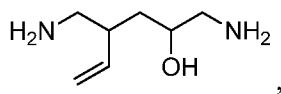
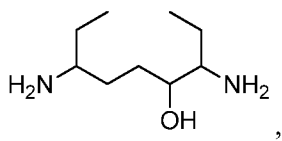
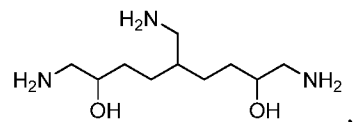
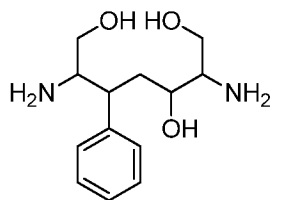
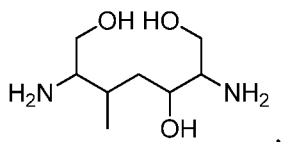
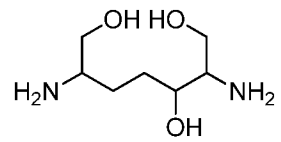
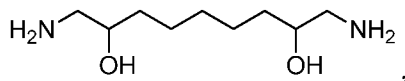
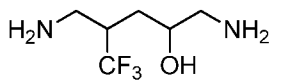
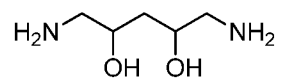
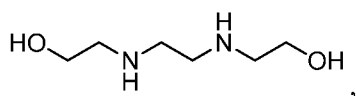
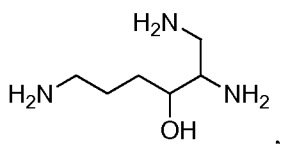
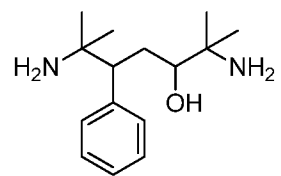
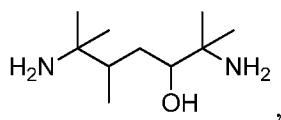
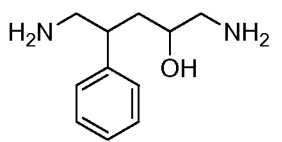
[0088] The surface topography of the synthesized membranes can be investigated by atomic force microscopy (AFM). Such investigation allows calculation of a root mean squared (RMS) roughness value for a membrane surface (Hoek *et al. Langmuir* **2003**, 19: 4836-4847). In one aspect, the thin film has a RMS roughness of less than 70 nm. For example, the thin film can have a RMS roughness of less than 60 nm, 50 nm, 40 nm, 30 nm, 20 nm, or 10 nm. In another aspect, the thin film can have a RMS roughness between 70 nm to 10 nm, such as, for example, between 70 nm and 30 nm.

[0089] While the thin film can be provided at any desired film thickness, the thin film of the invention are, in one aspect, provided at a thickness of from about 30 nm to about 300 nm. For example, the polyamide film can be provided at a thickness of from about 30 nm to about 50 nm, from about 90 nm to about 120 nm, from about 200 nm to about 230 nm, or from about 150 nm to about 200 nm.

(1) EXEMPLARY POLYAMINES

[0090] Below are non-limiting examples of polyamines of the formulas disclosed herein





g. INTERFACIAL FREE ENERGY OF WETTING

[0091] Wettability of Solid Surfaces. The classical definition of “lyophilic” or “wetting” is a liquid contact angle less than 90 degrees, whereas “lyophobic” or “non-wetting” is a liquid contact angle greater than 90 degrees. According to the Dupre equation, the solid-liquid interfacial free energy derives from the difference between the solid (1), liquid (3), and solid-liquid interfacial tensions. (A. Dupre, *Theorie Mecanique de la Chaleur*; Gauthier-Villars: Paris, 1869) The solid-liquid interfacial free energy is calculated directly from the liquid contact angle using the Young-Dupre equation,

$$-\Delta G_{13} = \gamma_3 \left(1 + \frac{\cos \theta_3}{r} \right), \quad (1)$$

which is derived by combining the Dupre equation with the Young equation. (T. Young, “An Essay on the Cohesion of Fluids,” *Philosophical Transactions of the Royal Society of London* **1805**, 95, 65-87). In fact, eq (1) is a modified form of the Young-Dupre equation that accounts for the excess interfacial area created by surface roughness as suggested by Wenzel. In eq (2), r is the actual surface area of a roughened solid surface, which can be derived from Atomic Force Microscopy (AFM) surface area difference (a.k.a., Wenzel’s “roughness factor” or the ratio of actual surface area to geometric surface area). (R. N. Wenzel, *Industrial and Engineering Chemistry* **1936**, 28, 988-994).

[0092] Components of Solid Surface Tension and their Determination. According to van Oss, the total surface tension of any media is the sum of apolar (Lifshitz-van der Waals) and polar (Lewis acid-base) components, or

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB}, \quad (2)$$

where $\gamma^{AB} (= 2\sqrt{\gamma^+ \gamma^-})$ is the acid-base component, γ^+ and γ^- are electron-acceptor and electron-donor components, and γ^{LW} is the Lifshitz-van der Waals component. (C. J. van Oss, *Interfacial Forces in Aqueous Media*; Marcel Dekker, Inc.: New York, NY, 1994). Individual surface tension components are determined from contact angles measured using three probe liquids of known surface tension and calculated by the extended Young equation,

$$\left(1 + \frac{\cos \theta}{r} \right) \gamma_l^{TOT} = 2 \left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right) \quad (3)$$

where θ is the equilibrium contact angle of a probe liquid on the surface, γ_l^{TOT} is the total liquid surface tension. The subscripts s and l represent the solid surface and the probe liquid, respectively.

[0093] Interfacial Free Energy, Hydrophilicity and Fouling Resistance. The interfacial free energy at contact, ΔG_{132}^{IF} , offers additional insight into the inherent stability of a solid material (1) interacting through a liquid media (3) with another solid material (2). It accounts for interactions between the two solid surfaces, between water molecules and each of the solid surfaces, and among water molecules themselves. The interfacial free energy gives an indication of the thermodynamic tendency of the surfaces to be attracted or repelled by one another and is determined from, (D. Myers, *Surfaces, Interfaces, and Colloids: Principles and Applications*; 2nd ed.; John Wiley & Sons: New York, NY, 1999)

$$\Delta G_{132}^{IF} = \Delta G_{132}^{LW} + \Delta G_{132}^{AB}, \quad (4a)$$

$$\Delta G_{132}^{LW} = 2 \left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}} \right) \left(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}} \right), \quad (b)$$

$$\Delta G_{132}^{AB} = 2\sqrt{\gamma_3^+} \left(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-} \right) + 2\sqrt{\gamma_3^-} \left(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+} \right) - 2\sqrt{\gamma_1^+ \gamma_2^-} - 2\sqrt{\gamma_1^- \gamma_2^+}. \quad (c)$$

[0094] If surface 1 and 2 are the same material (i.e., $2 = 1$), ΔG_{131}^{IF} indicates the interfacial free energy of cohesion at contact. This is the most fundamental thermodynamic definition of “hydrophilicity” and “hydrophobicity”. The term “hydrophilicity” and “corrected interfacial free energy of wetting” and the like terms, as used herein, refer to is the interfacial free energy of cohesion at contact as determined by the value of ΔG_{131}^{IF} . ΔG_{131}^{IF} is measured in mJ/m^2 .

[0095] Polymers containing polar functional groups (most often O, N, S, and P containing moieties) are sometimes described and thought of as hydrophilic. In the case of membranes, the term “hydrophilic” is often used synonymously with “fouling resistant” but there has been some confusion in the literature about apparently hydrophilic polymers (according to classical definitions of wettability and hydrophilicity) being somewhat fouling prone (e.g., PSf, PES, PC, and PEI). Perhaps for water treatment membranes, a special case should be considered. van Oss points out that when two materials with significant mixed

polar functionality (i.e., seemingly “hydrophilic” but containing both electron donor and electron acceptor) that they can be thermodynamically attracted to one another through Lewis acid-base attraction (see eq. 4c). (C. J. van Oss, *The Properties of Water and their Role in Colloidal and Biological Systems*; Academic Press/Elsevier Ltd.: New York, NY, 2008) Through the third and fourth terms of eq. 4c, such materials can introduce negative AB interfacial free energy, and in particular, when the electron donor or acceptor surface tension components of either of the solid materials are less than those of water. This phenomenon affects both the free energy of cohesion and adhesion; hence, seemingly “hydrophilic” materials may actually produce negative “hydrophobic” free energies of cohesion or adhesion.

[0096] In one aspect, the thin film has a water contact angle of less than 40 degrees. For example, the thin film can have a water contact angle of less than 30 degrees, 25 degrees, 20 degrees, 15 degrees, 10 degrees, or 5 degrees. For example, the thin film can have a water contact angle between 40 degrees and 5 degrees.

[0097] In one aspect, the thin film has a roughness corrected interfacial free energy of wetting more negative than -100 mJ/m^2 . For example, the thin film can have a roughness corrected interfacial free energy of wetting more negative than -110 mJ/m^2 , -120 mJ/m^2 , -130 mJ/m^2 , -140 mJ/m^2 , -150 mJ/m^2 , or -180 mJ/m^2 .

[0098] In another aspect, the thin film can have a roughness corrected interfacial free energy of wetting between -100 mJ/m^2 and -180 mJ/m^2 . For example, the thin film can have a roughness corrected interfacial free energy of wetting between -100 mJ/m^2 and -150 mJ/m^2 or between -100 mJ/m^2 and -130 mJ/m^2 .

3. CROSSLINKED POLYVINYL ALCOHOL FILM

[0099] In one aspect, a second film is coated on the thin film, wherein the second film comprises crosslinked polyvinyl alcohol film. In one aspect, the second film can be polymerized on the thin film. In another aspect, the polyvinyl alcohol film can be deposited on the thin film. Deposition techniques includes various types of film casting, such as, spin coating or dipping.

[00100] In one aspect, to maintain stability and to produce adequate selectivity in molecular separations, the second films described herein can be cross-linked. In a further

aspect, the second can be a poly(vinyl alcohol) film. The crosslinking agents can include, but are not limited to, succinic acid (>99%), maleic acid (>99%), malic acid (>99%), glutaraldehyde (25% aqueous 6 solution) and suberic acid (>99%). . Crosslinking agents can be obtained commercially, for example, from the Sigma-Aldrich company (St. Louis, Missouri, USA). In a still further aspect, the second film can have a degree of crosslinking of about 10 percent to about 80 percent. For example, the second film can have a degree of crosslinking of about 30 percent to about 80 percent, or about 40 percent to about 70 percent.

[00101] In one aspect, the second film has a water contact angle less than 40 degrees. For example, the second film can have a water contact angle of less than 30 degrees, 25 degrees, 20 degrees, 15 degrees, 10 degrees, or 5 degrees. For example, the second film can have a water contact angle between 40 degrees and 5 degrees.

[00102] While the second film can be provided at any desired film thickness, the second films of the invention are, in one aspect, provided at a thickness of from about 10 nm to about 1000 nm, from about 100 nm to about 1000 nm, from about 1 nm to about 500 nm, from about 10 nm to about 500 nm, from about 50 nm to about 500 nm, from about 50 nm to about 200 nm, from about 50 nm to about 250 nm, from about 50 nm to about 300 nm, or from about 200 nm to about 300 nm..

[00103] The film thickness can be visually confirmed and quantified, for example, by using transmission electron microscopy (TEM). See, *i.e.*, Freger, V., et al. (2002) "TFC polyamide membranes modified by grafting of hydrophilic polymers: an FT-IR/AFM/TEM study," *Journal of Membrane Science* **209**: 283-292.

[00104] For example, the second film can be made by dissolving poly(vinyl alcohol) powder in deionized water at 90 °C using mechanical stirring (Fisher Scientific, Pittsburgh, PA, USA) for about 60 minutes to make poly(vinyl alcohol) aqueous solutions. The poly(vinyl alcohol) molecular weight can be, but is not limited to 47 kDa and the poly(vinyl alcohol) concentration can be, but is not limited to, 0.10 wt . Next, poly(vinyl alcohol) solutions can be cooled to room temperature and the crosslinking agent can be added, along with 2 M HCl as catalyst, under continuous stirring to produce the poly(vinyl alcohol) casting solution. Crosslinking agent concentration can be selected to produce a theoretical crosslinking degree of about less than 10 percent, about 10 percent, about 20 percent, about

30 percent, about 40 percent, about 50 percent, about 60 percent, about 70 percent, about 80 percent, or about greater than 80 percent, as calculated by equation 1 herein.

[00105] In one aspect, a poly(vinyl alcohol) casting solution can be coated onto a thin film one time, two time, three times, or greater than three times. First, the casting solution can be poured onto the thin film and can sit for about 10 minutes. Then, the solute can be drained and the remaining water can be allowed to evaporate at room temperature for about 24 h. Next, the coated membrane can be dropped into the same poly(vinyl alcohol) solution for about 10 seconds and then taken out, and air-dried for 24 hours. The 10- second coating and drying can be repeated a third time to produce a defect-free, ultra-thin poly(vinyl alcohol) coating film. The poly(vinyl alcohol) coated thin film can then be cured at 100 °C for about 10 minutes.

4. REVERSE OSMOSIS MEMBRANES

[00106] In one aspect, the membranes of the invention can be reverse osmosis membranes, including thin film composite (TFC) membranes. Among particularly useful membranes for osmosis applications are those in which the semi-permeable or discriminating layer is a polyamide. A thin film composite membrane typically comprises a porous support and a semi-permeable polymer film polymerized on the porous support.

[00107] Composite polyamide membranes are typically prepared by coating a porous support with a polyfunctional amine monomer, most commonly coated from an aqueous solution. Although water is a preferred solvent, non-aqueous solvents can be utilized, such as acetonitrile and dimethylformamide (DMF). A polyfunctional acyl halide monomer (also referred to as acid halide) is subsequently coated on the support, typically coated first on the porous support followed by the acyl halide solution. Although one or both of the polyfunctional amine and acyl halide can be applied to the porous support from a solution, they can alternatively be applied by other means such as by vapor deposition, or heat.

[00108] The resultant semi-permeable membrane can then be employed in a method of purifying or separating various liquids, such as water. Such a method typically comprises applying pressure to a water solution (e.g., a salt water solution) on the polymer matrix film side of the membrane; and collecting purified water on the other side of the membrane.

5. PROPERTIES OF MEMBRANES

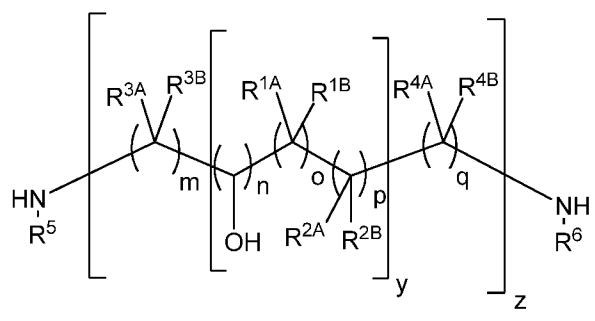
[00109] In various aspects, the disclosed membranes can have various properties that provide the superior function of the membranes, including excellent flux, improved hydrophilicity, improved resistance to fouling, higher porosity, tunable surface charge properties, and higher thermal stability. It is also understood that the membranes have other properties.

[00110] For example, the membrane can have a roughness corrected interfacial free energy of wetting between -100 mJ/m^2 and -180 mJ/m^2 and have a RMS roughness of less than 70 nm. Such membrane will have a high resistance of fouling.

[00111] In one aspect, the membrane does not substantially degrade upon exposure to 200 ppm NaOCl for 24 hours. Substantial degradation corresponds to a greater than 10 percent increase or decrease in the hydraulic permeability and/or salt permeability. In another aspect, the membrane does not substantially degrade upon exposure to 200 ppm NaOCl for 3 days. In yet another aspect, the membrane does not substantially degrade upon exposure to 200 ppm NaOCl for 1 week.

C. METHODS FOR PREPARING FILTRATION MEMBRANES

[00112] In one aspect, the invention relates to a method for preparing a chlorine-tolerant membrane, the method comprising the steps of: a) providing, on the surface of a porous support membrane, a composition comprising: i) a polyamine having the structure of Formula I:



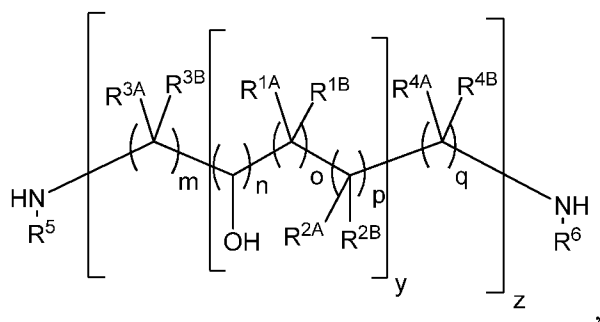
wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $\text{C}=\text{O}$;

wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6; ii) a polyfunctional acyl halide; (b) polymerizing the polyamine and the polyfunctional acyl halide on the surface of the porous support membrane, thereby producing a thin film; and c) a coating of a second film on the thin film, wherein the second film comprises crosslinked polyvinyl alcohol film.

[00113] In one aspect, the second film can be polymerized on the thin film. In another aspect, the polyvinyl alcohol film can be deposited on the thin film. Deposition techniques includes various types of film casting, such as, spin coating or dipping.

D. METHODS FOR PURIFYING LIQUIDS

[00114] In one aspect, the invention relates to a water purification method, the method comprising the step of: a) filtering water through a membrane, wherein the membrane comprises: i) a porous support membrane; ii) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure:



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$; wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$; wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, or $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio; wherein m is an integer from 1-6; wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen; wherein o is an integer from 0-6; wherein p is an integer from 0-6; wherein q is an integer from 1-6; wherein y is an integer from 1-6; and wherein z is an integer from 1-6; wherein the water comprises at least 10 ppm of chlorine.

[00115] In one aspect, the thin film is coated with a second film comprising crosslinked polyvinyl alcohol film. Such second films are described elsewhere herein.

[00116] In one aspect, the method is performed for at least 24 hours. For example, the method can be performed for at least 3 days, one week, one month, three months, or six months.

[00117] In one aspect, the filtering is reverse osmosis filtering. Thus, the membranes disclosed herein can be used for reverse osmosis separations including seawater desalination, brackish water desalination, surface and ground water purification, cooling tower water hardness removal, drinking water softening, and ultra-pure water production.

[00118] In one aspect, the filtering comprises applying pressure to the water.

[00119] In one aspect, the water further comprises one solute.

[00120] In one aspect, the water comprises at least 20 ppm, 30 ppm, 40 ppm, 50 ppm, 60 ppm, 70 ppm, 80 ppm, 90 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm, 400 ppm, or 500 ppm of chlorine. For example, the water can comprise from 10 ppm to 500 ppm of chlorine, such as from 10 ppm to 200 ppm of chlorine.

[00121] In one aspect, the method further comprises collecting the purified water.

[00122] The feasibility of a membrane separation process is typically determined by stability in water flux and solute retention with time. Fouling, and in particular biological fouling, can alter the selectivity of a membrane and causes membrane degradation either directly by microbial action or indirectly through increased cleaning requirements. These characteristics can have a direct effect on the size of the membrane filtration plant, the overall investment costs, and operating and maintenance expenses. By applying the membranes and methods disclosed herein to commercial membrane and desalination processes, the overall costs can be significantly reduced due to the improved selectivity and fouling resistance of the nanocomposite membranes of the invention. Due to antibiotic properties of the nanoparticles, in particular silver-exchanged Zeolite A nanoparticles, disposed within the nanocomposite membranes, less frequent chemical cleanings and lower operating pressures are typically required, thereby offering additional savings to owners and operators of these processes.

[00123] The membranes can have a first face and a second face. The first face of the membrane can be contacted with a first solution of a first volume having a first salt concentration at a first pressure; and the second face of the membrane can be contacted with a second solution of a second volume having a second salt concentration at a second pressure. The first solution can be in fluid communication with the second solution through the membrane. The first salt concentration can then be higher than the second salt concentration,

thereby creating an osmotic pressure across the membrane. The first pressure can be sufficiently higher than the second pressure to overcome the osmotic pressure, thereby increasing the second volume and decreasing the first volume.

[00124] In various further aspects, the membranes disclosed herein can be used for reverse osmosis separations including liquids other than water. For example, the membranes can be used to remove impurities from alcohols, including methanol, ethanol, n-propanol, isopropanol, or butanol. Typically, suitable liquids are selected from among liquids that do not substantially react with or solvate the membranes.

E. EXPERIMENTAL

[00125] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

1. PERMEABILITY OF POLYAMIDE-BASED MEMBRANES

[00126] Meta-phenylenediamine (MPD)-TMC polyamides degrade upon exposure to 200 ppm NaOCl for 18 h (both water and salt permeability increase relative to the as-cast membrane) (FIG. 2). The deformation of the MPD-based polyamide is likely due to the sodium hypochlorite, loosening the thin film and decreasing selectivity. In contrast, the DAP-TMC membrane's water and salt permeability decrease upon the same NaOCl exposure. While the tightening of the DAP-TMC membrane is unexpected, it is encouraging because the salt rejection did not decline suggesting it is indeed chlorine tolerant. The decrease in the DAP-based membrane's salt permeability may be from chlorination of unreacted diamine entrapped in the film. Therefore, chemical post-treatments may be required to release residual, unreacted diamine from the DAP-TMC films to encourage inter-chain hydrogen bonding.

2. SURFACE TOPOGRAPHY OF POLYAMIDE-BASED MEMBRANES

[00127] SEM images of as-cast MPD-TMC and DAP-TMC composite membrane coating films are depicted in FIG. 3A and 3B, respectively. The DAP-based membrane image is at 35k X magnification, whereas the MPD-based membrane is at 25k X magnification. The subtle roughness features on the DAP-based membrane are from the sputter coating applied to make the surface of the membrane sample conducting, which aids in SEM imaging; while the MPD-based film exhibits the classical lobe-like morphology of polyamide RO membranes while the DAP based film appears to be molecularly smooth. Moreover, the pure water contact angle of the MPD-based membrane was 58 °C, while that of the DAP-based membrane was 35 °C. The roughness corrected interfacial free energy of wetting (Gosh, A. K., et al. (2008) *J. Membr. Sci.* **311**: 34–45) for the DAP and MPD membranes are -132 and -99 mJ/m², respectively, indicating the DAP-based membrane is significantly more hydrophilic. These results are also encouraging because it is generally believed that RO membranes with smoother, more hydrophilic surfaces are more fouling-resistant.

3. PREPARATION OF POLYAMIDE-BASED MEMBRANES

[00128] The DAP/guanazole-based membranes are formed through the interfacial polymerization of either diamine with TMC. Briefly, an asymmetric membrane polymer support is saturated in an aqueous solution containing the chosen diamine, the saturated support membrane is then contacted with the TMC solution to form a thin film on the surface of the support membrane through interfacial polymerization, and the thin film covered support membrane is then cured at high temperature to form the final thin film composite membrane.

[00129] 0.1 wt % TMC was dissolved in Isopar (400 g total solution). 2 wt% of the diamine was then dissolved in water, generating 200 g of the total solution. The polysulfone membrane support was taped to a glass plated. After approximately 2 h, both the diamine and TMC appeared to have dissolved. At this time, the diamine solution was poured into a saturation bath. The support membrane was saturated in the solution for 2 min. The saturated support membrane (on the glass plate) was then removed from the saturation bath, and excess solution removed from the surface of the membrane using an air knife (5 psi). Next, the TMC solution was poured into the vertical holder and the membrane placed in this solution. The membrane remained in the solution for 2 min, to allow the coating film to

form. At this time the support membrane was removed from the TMC solution and held vertically for 2 min. The membrane was then removed from the glass plate and placed in an oven (at 90 °C) for 15 min, before being placed in a 0.2 wt% sodium carbonate solution for 2 h.

[00130] Please note that the reagent weight percents listed are for brackish water application (2 g/L NaCl feed solution tested at 225 psi). There remains the potential to explore a range of polymerization conditions. For example, the DAP and guanazole diamines have different diffusivity and solubility in organic solvents than MPD; hence, the interfacial polymerization reaction conditions (diamine concentrations, acylation catalysts, miscibility enhancers, immersion times, air knife pressure, solvent, temperature, wet/dry curing, and other physical/chemical post-treatments) could be varied in order to modulate the thickness (i.e., diffusion path length) and extent of cross-linking (i.e., free volume and hydrophilicity) of the coating film, which directly influence solvent and solute solubility and diffusivity (i.e., permeability) in RO membranes.

[00131] Upon scale-up, the DAP or guanazole membranes can be fabricated on a membrane production line similar to existing polyamide based NF and RO membranes. These membranes would be formed as flat sheet or hollow fiber type membranes and packaged in modules for use in existing and new water treatment installations.

[00132] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other aspects of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

F. REFERENCES

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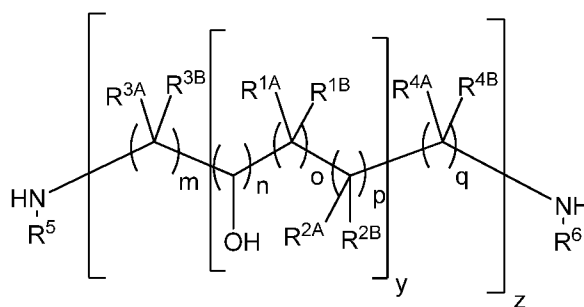
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CLAIMS

What is claimed is:

1. A water purification method comprising the step of:
 - (a) filtering water through a membrane, wherein the membrane comprises:
 - (i) a porous support membrane;
 - (ii) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure



wherein each of $\text{R}^{1\text{A}}$ and $\text{R}^{1\text{B}}$ is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein $\text{R}^{1\text{A}}$ and $\text{R}^{1\text{B}}$ together is $\text{C}=\text{O}$;

wherein each of $\text{R}^{2\text{A}}$ and $\text{R}^{2\text{B}}$ is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein $\text{R}^{2\text{A}}$ and $\text{R}^{2\text{B}}$ together is $\text{C}=\text{O}$;

wherein each of $\text{R}^{3\text{A}}$ and $\text{R}^{3\text{B}}$ is independently selected from hydrogen, alkyl, or $-\text{CH}_2\text{OH}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein each of $\text{R}^{4\text{A}}$ and $\text{R}^{4\text{B}}$ is independently selected from hydrogen, alkyl, and $-\text{CH}_2\text{OH}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein R^5 is selected from hydrogen and $-\text{alkyl-hydroxyl}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein R^6 is selected from hydrogen and $-\text{alkyl-hydroxyl}$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein m is an integer from 1-6;

wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R⁵ and R⁶ are hydrogen;

wherein o is an integer from 0-6;

wherein p is an integer from 0-6;

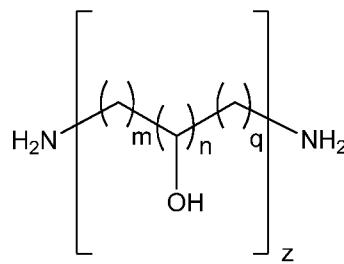
wherein q is an integer from 1-6;

wherein y is an integer from 1-6; and

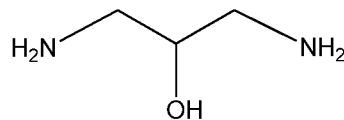
wherein z is an integer from 1-6;

wherein the water comprises at least 10 ppm of chlorine.

2. The method of claim 1, wherein the polyamine has the structure

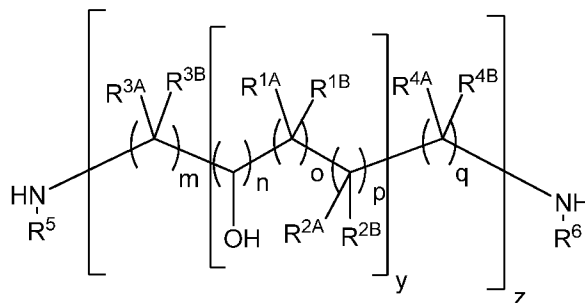


3. The method of claims 1 or 2, wherein the polyamine has the structure



4. The method of any one of claims 1-3, wherein R^{3A} and R^{3B} are hydrogen, wherein R^{4A} and R^{4B} are hydrogen, R⁵ is hydrogen, wherein R⁶ is -alkyl-hydroxyl and is substituted with 0 groups, wherein m is 1, wherein n is 0, wherein o is 0, wherein p is 0, wherein q is 1, wherein y is 1, and wherein z is 1.
5. The method of any one of claims 1-3, wherein R^{1A} and R^{1B} are hydrogen, wherein R⁵ is hydrogen, wherein R⁶ is hydrogen, wherein m is 1, wherein n is 1, wherein o is 1, wherein p is 1, wherein q is 1, wherein y is 1, and wherein z is 1.
6. The method of any one of claims 1-5, wherein the porous support membrane comprises polysulfone polyethersulfone, polyaniline, or polyacrylonitrile, or a combination thereof.
7. The method of any one of claims 1-6, wherein the thin film is coated with a second film comprising crosslinked polyvinyl alcohol film.
8. The method of claim 7, wherein the polyvinyl alcohol film has a crosslinking degree of about 10 percent to about 80 percent.
9. A chlorine-tolerant membrane comprising:

- (a) a porous support membrane,
 (b) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$;

wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$;

wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein m is an integer from 1-6;

wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen;

wherein o is an integer from 0-6;

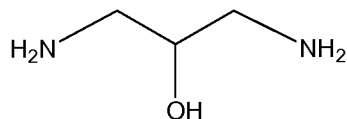
wherein p is an integer from 0-6;

wherein q is an integer from 1-6;

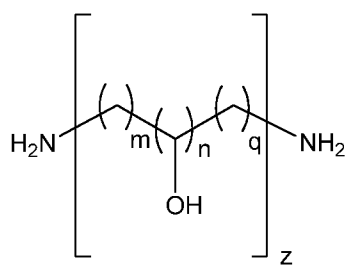
wherein y is an integer from 1-6; and

wherein z is an integer from 1-6.

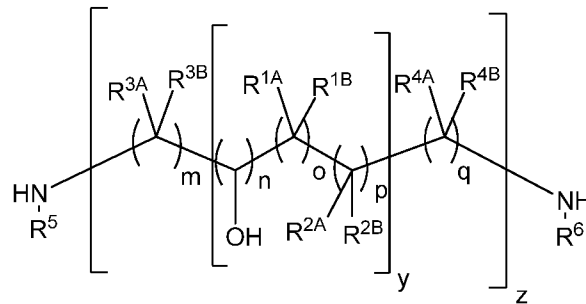
10. The chlorine-tolerant membrane of claim 9, wherein the polyamine is not



11. The chlorine-tolerant membrane of claims 9 or 10, wherein the polyamine has the structure



12. The chlorine-tolerant membrane of claim 9, wherein at least one of R^{1A} , R^{1B} , R^{2A} , or R^{2B} is not hydrogen.
13. The chlorine-tolerant membrane of claims 9 or 12, wherein R^{3A} and R^{3B} are hydrogen, wherein R^{4A} and R^{4B} are hydrogen, R^5 is hydrogen, wherein R^6 is -alkyl-hydroxyl and is substituted with 0 groups, wherein m is 1, wherein n is 0, wherein o is 0, wherein p is 0, wherein q is 1, wherein y is 1, and wherein z is 1.
14. The chlorine-tolerant membrane of claims 9 or 12, wherein R^{1A} and R^{1B} are hydrogen, wherein R^5 is hydrogen, wherein R^6 is hydrogen, wherein m is 1, wherein n is 1, wherein o is 1, wherein p is 1, wherein q is 1, wherein y is 1, and wherein z is 1.
15. The chlorine-tolerant reverse osmosis membrane of any one of claims 9-14, wherein the thin film has a root mean square (RMS) roughness of less than 70 nm.
16. The chlorine-tolerant reverse osmosis membrane of any one of claims 9-15, wherein the thin film has a roughness corrected interfacial free energy of wetting more negative than -100 mJ/m^2 .
17. A chlorine-tolerant membrane comprising:
- (a) a porous support membrane,
 - (b) a thin film layered on a surface of the support membrane, wherein the film is produced by the reaction of (i) a polyfunctional acyl halide with (ii) a polyamine having the structure



wherein each of R^{1A} and R^{1B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{1A} and R^{1B} together is $C=O$;

wherein each of R^{2A} and R^{2B} is independently selected from hydrogen, alkyl, alkenyl, alkynyl, amino, hydroxyl, halo, and thio, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio, or wherein R^{2A} and R^{2B} together is $C=O$;

wherein each of R^{3A} and R^{3B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein each of R^{4A} and R^{4B} is independently selected from hydrogen, alkyl, and $-CH_2OH$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein R^5 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein R^6 is selected from hydrogen and $-alkyl-hydroxyl$, and is substituted with 0, 1, 2, or 3 groups selected from alkyl, amino, hydroxyl, halo, and thio;

wherein m is an integer from 1-6;

wherein n is an integer from 0-6, wherein n is an integer from 1-6 if both R^5 and R^6 are hydrogen;

wherein o is an integer from 0-6;

wherein p is an integer from 0-6;

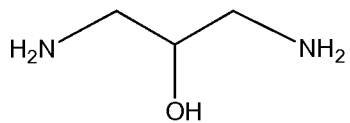
wherein q is an integer from 1-6;

wherein y is an integer from 1-6; and

wherein z is an integer from 1-6; and

(c) a coating on the thin film, wherein the coating is a crosslinked polyvinyl alcohol film.

18. The chlorine-tolerant reverse osmosis membrane of claim 17, wherein the polyamine has the structure



19. The chlorine-tolerant membrane of claims 17 or 18, wherein the polyvinyl alcohol film has a crosslinking degree of about 10 percent to about 80 percent.
20. The chlorine-tolerant membrane of any one of claims 17-19, wherein the polyvinyl alcohol film is polymerized on the thin film.

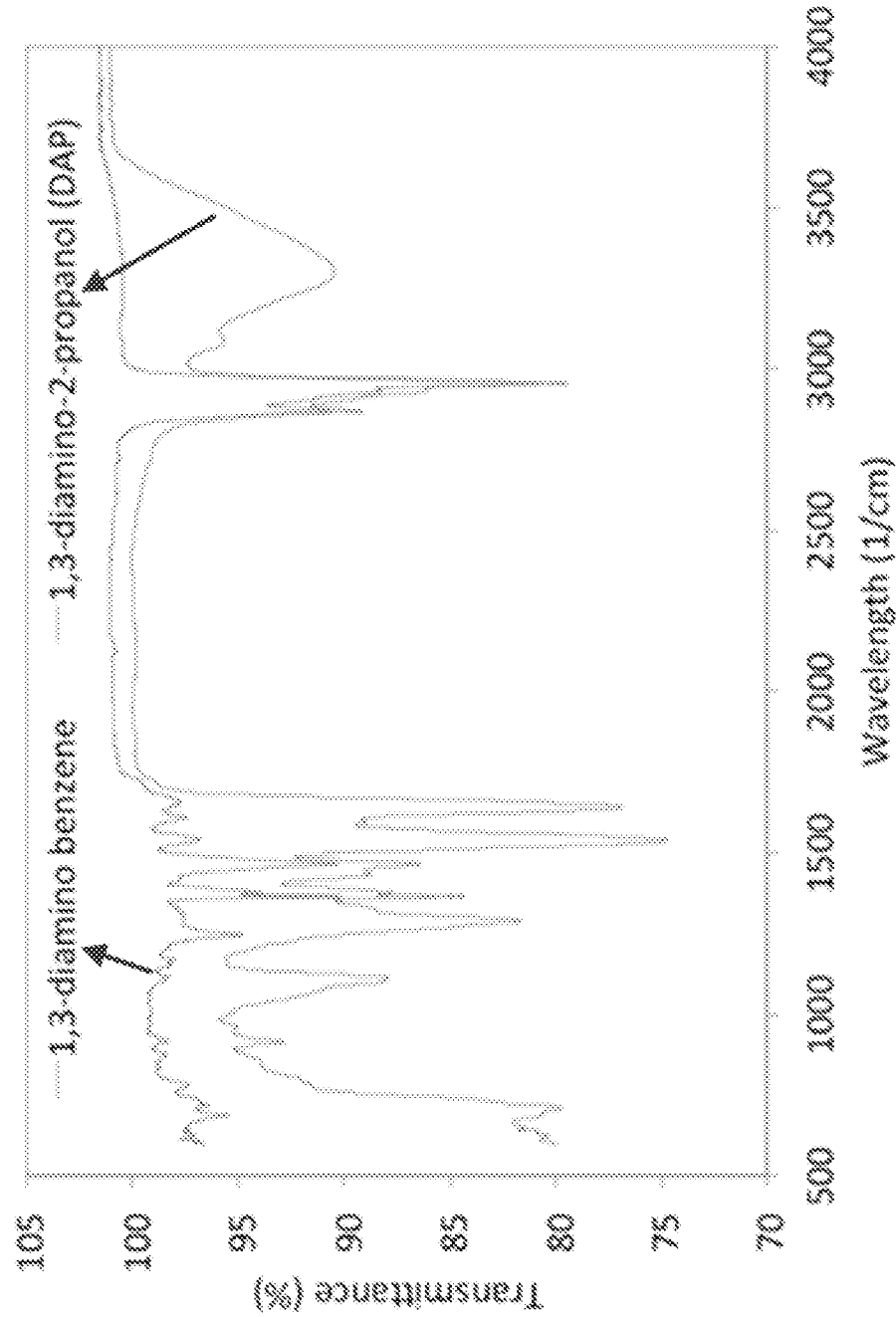


FIG. 1

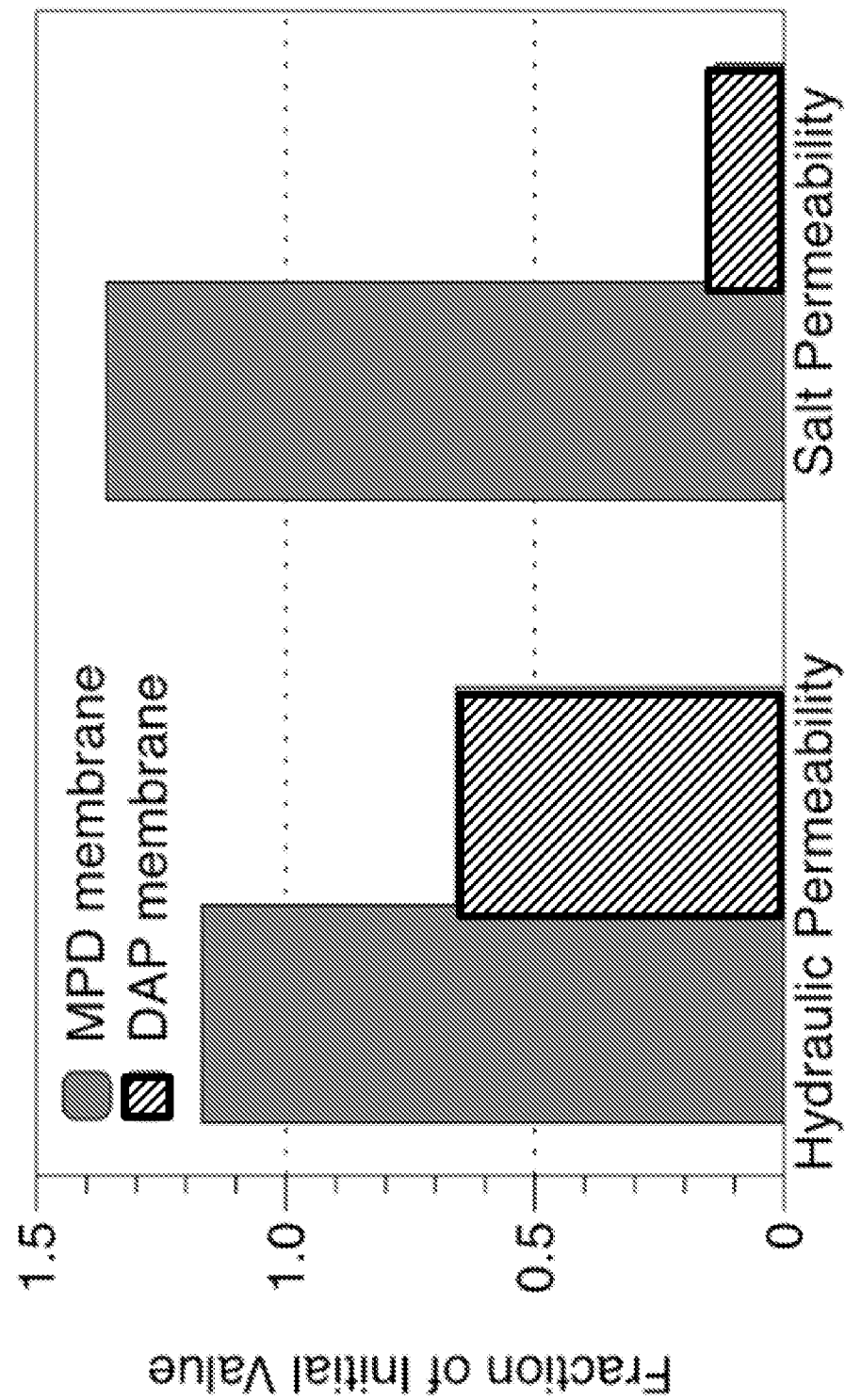


FIG. 2

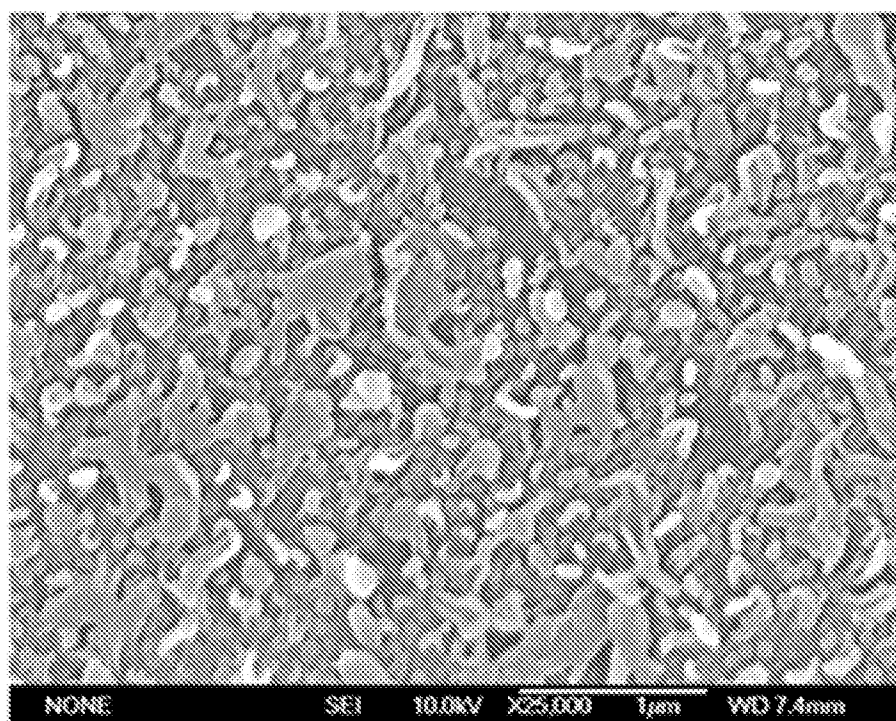


FIG. 3A

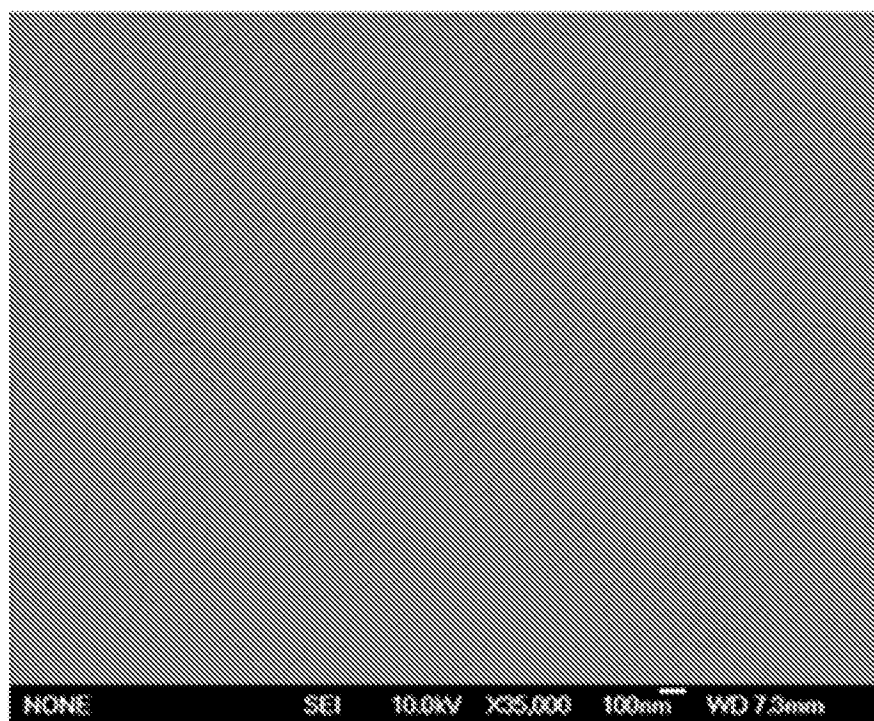


FIG. 3B