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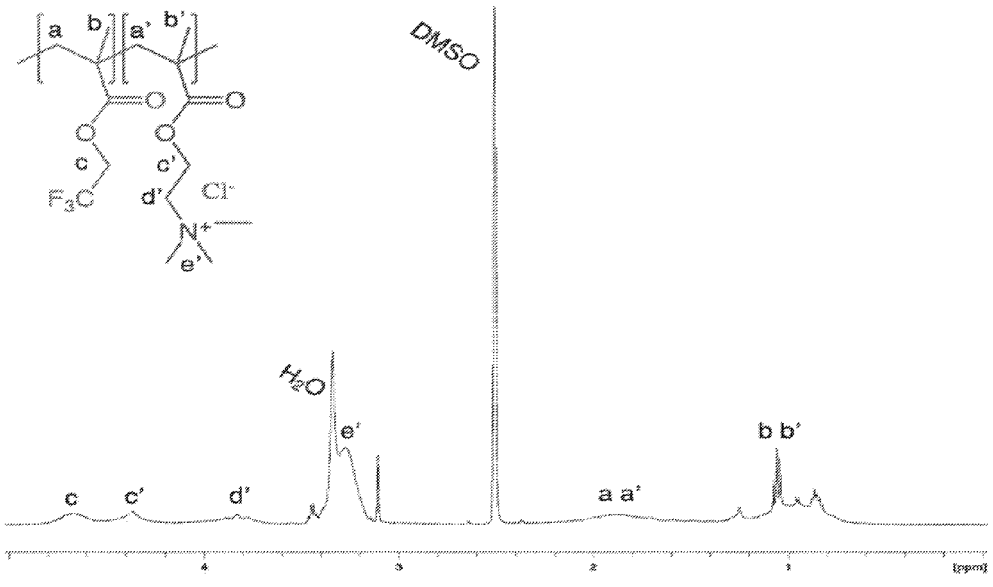
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FIG. 1



(57) **Abstract:** Disclosed are composite membranes comprising a porous support and a selective layer comprising a first copolymer and a second copolymer wherein: the first copolymer comprises a first plurality of hydrophobic repeat units and a plurality of cationic repeat units; and the second copolymer comprises a second plurality of hydrophobic repeat units and a plurality of anionic repeat units. Also disclosed are methods of fabricating and using the composite membranes.

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AMPHIPHILIC POLYELECTROLYTE COMPLEXES, MULTILAYERS AND BLENDS

RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Patent Application No. 63/325,274, filed March 30, 2022, the contents of which are hereby incorporated by reference in their entirety.

GOVERNMENT SUPPORT

This invention was made with government support under grant number DEFE003185 awarded by the Department of Energy, and grant number 1553661 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

One of the most energy consuming activities in the chemical industry is separating chemical compounds. Membranes are excellent candidates for achieving efficient separations: they are scalable, energy efficient, and already widely used in gas and liquid separation processes. Nonetheless, their broader use is limited by the separation capabilities, fouling, and stability of membranes prepared by conventional methods.

Presently, the separation of similarly sized molecules is achieved by using highly energy-intensive methods, such as, chromatography, distillation, and extraction. For example, the purification of propane and ethene alone accounts for 0.3% of the global energy consumption. Utilizing membranes instead of current methods for these challenging separations would significantly reduce energy consumption while increasing the sustainability of these processes. Other separations, such as benzene derivatives from each other and the isolation of bioactive compounds with added value, are potential processes where membranes could be used.

In addition to limitations on selectivity, membrane fouling severely limits the broader use of membranes in applications where feeds have high concentrations of components such as biomacromolecules, particulates, and/or oil. Therefore, it is crucial to consider fouling prevention in designing novel membrane materials. Fouling is one of the most relevant fields of study in membrane filtration and is a major obstacle to improving the performance of membrane separation processes.[6] Fouling has detrimental effects on the performance and integrity of membranes. Given the limitations of commercial membranes against foulants,

being able to tune membrane properties like permeance, pore size, and selectivity, while maintaining easy manufacturability and high fouling resistance could transform the water filtration field.

Lastly, membranes with higher selectivity can improve the economic feasibility of membrane processes for many applications. For instance, membranes with tunable pore size and charge at the nanometer scale could be useful in bioseparations, treating complex wastewaters, selective removal of organics (*e.g.,* dyes) and other contaminants from solutions for reuse, water softening, pretreatment of seawater for desalination by reverse osmosis (RO), and final treatment of secondary and tertiary wastewater effluents. In all these cases, it is essential for selectivity to be paired with fouling resistance.

Previous research has demonstrated that random zwitterionic amphiphilic copolymer (r-ZAC) membranes can be formed via the self-assembly of zwitterionic nanodomains acting as a network of effective nanochannels for water permeation. The main characteristics of r-ZAC membranes include excellent fouling resistance, a ~1-1.5 nm size cutoff, and low salt ion retention. However, while various zwitterionic monomers can be synthesized, only a handful are commercially available, some from only one supplier. Moreover, most zwitterionic monomers exhibit poor solubility in many solvents, further adding to their synthesis challenges. As a result, the range of r-ZAC chemistries that can feasibly be converted to membranes produced at a large scale are limited. Ionic or ionizable monomers, on the other hand, are widely available, cheaper, and typically easier to solubilize and synthesize.

Another class of selective layers that has gained attention in the past decade are polyelectrolyte multilayers, these selective layers are built by layer-by-layer (LBL) deposition of oppositely charged polyelectrolytes. A multilayer approach that allows the development of membranes based on the formation of polyelectrolyte complexes between multiple oppositely charged water soluble homopolymers. Although these membranes have shown good membrane performance, especially in the removal of micropollutants, there is no significant research on their uncrossed-linked long term stability. Additionally, their fabrication method requires multiple steps and would be complex to scale up. These coatings are typically fabricated several rounds of dip- or spray-coating of alternating anionic and cationic, water-soluble polyelectrolytes, separated by rinses. Typically, at least 3-5 bilayers are needed (so 12-20 dip or spray steps).

SUMMARY OF THE INVENTION

In one aspect, the present disclosure provides composite membranes, comprising a porous support; and a selective layer comprising a first copolymer and a second copolymer; wherein:

the first copolymer comprises a first plurality of hydrophobic repeat units and a plurality of cationic repeat units;

the second copolymer comprises a second plurality of hydrophobic repeat units and a plurality of anionic repeat units; and

the first copolymer and the second copolymer are essentially insoluble in water (*e.g.*, under operating conditions).

In another aspect, the present disclosed provides methods of separating a solute from a solution comprising contacting the solution with a composite membrane disclosed herein.

In another aspect, the present disclosure provides methods of fabricating a composite membrane disclosed herein comprising applying a first copolymer, as disclosed herein, and a second copolymer, as disclosed herein, to a porous support, thereby fabricating a composite membrane disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an NMR spectrum of A+ chemical structure indicating copolymerization of two monomer units.

FIG. 2 shows an NMR spectrum of S- chemical structure indicating copolymerization of the two monomer units.

FIG. 3 shows a SEM image of **SA** coated on top of PS35.

FIG. 4 shows the rejection of neutral dyes by all membranes.

FIG. 5 shows the S-curves using neutral solutes.

FIG. 6 shows Na_2SO_4 rejections at different concentrations.

FIG. 7 shows Na_2SO_4 rejections at different concentrations.

FIG. 8 shows Na_2SO_4 rejections at different concentrations.

FIG. 9 shows $MgCl_2$ rejections at different concentrations.

FIG. 10 shows $MgCl_2$ rejections at different concentrations.

FIG. 11 shows $MgCl_2$ rejections at different concentrations.

FIG. 12 shows NaCl rejections at different concentrations.

FIG. 13 shows NaCl rejections at different concentrations.

FIG. 14 shows NaCl rejections at different concentrations.

FIG. 15 shows an oil-in-water 5 h fouling test of S- and SA. The initial flux of these membranes was set at 10 $L/m^2.h$.

FIG. 16 shows an NMR spectrum of M- chemical structure depicting the copolymerization of the two monomer units.

FIG. 17 shows a SEM image of **AM** coated on top of PS35.

FIG. 18 shows a SEM image of **70/30** coated on top of PS35.

FIG. 19 shows the water permeance of different APEC blend layers.

FIG. 20 show vitamin B12 rejection using different APEC blend layers.

FIG. 21 shows Na_2SO_4 rejections at different concentrations.

FIG. 22 shows $MgCl_2$ rejections at different concentrations.

FIG. 23 shows NaCl rejections at different concentrations.

FIG. 24 shows an NMR spectrum of **A2+** chemical structure indicating copolymerization of the two monomer units.

FIG. 25 shows an NMR spectrum of **S-** chemical structure indicating copolymerization of the two monomer units.

FIG. 26 shows an SEM image of **A2S** coated on top of PS35.

FIG. 27 shows the rejection of neutral dyes by **A2S,** AS, and control membranes.

FIG. 28 shows S-curves using neutral solutes.

FIG. 29 shows Na_2SO_4 rejections at different concentrations.

FIG. 30 shows $MgCl_2$ rejections at different concentrations.

FIG. 31 shows NaCl rejections at different concentrations.

FIG. 32 shows an NMR spectrum of **A+** chemical structure indicating copolymerization of the two monomer units.

FIG. 33 shows an NMR spectrum of **S2-** chemical structure indicating copolymerization of the two monomer units.

FIG. 34 shows an SEM image of **AS2** coated on top of PS35.

FIG. 35 shows the Rejection of neutral dyes by **AS2,** AS, and control membranes.

FIG. 36 shows Na_2SO_4 rejections at different concentrations.

FIG. 37 shows $MgCl_2$ rejections at different concentrations.

FIG. 38 shows NaCl rejections at different concentrations.

DETAILED DESCRIPTION OF THE INVENTION

Disclosed are thin film composite (TFC) membranes, wherein a thin "selective layer" is coated onto a porous support, where this selective support comprises a combination of at least two copolymers:

1) A "cationic copolymer" comprising at least two types of repeat units: a *hydrophobic* repeat unit whose homopolymer would be insoluble in water, and a *cationic* repeat unit which becomes at least partially positively charged when in water,
2) An "anionic copolymer" comprising at least two types of repeat units: a *hydrophobic* repeat unit as above, and an *anionic* repeat unit which becomes at least partially negatively charged when in water.

In certain preferred embodiments, both of the copolymers are essentially insoluble in water under use conditions. Typically each copolymer contains ~5-80 wt% of the charged (anionic or cationic) repeat units, more preferably 15-75% of the charged repeat units, and more preferably 30-60% of the charged repeat units. This feature, for example, differentiates the technology from polyelectrolyte multilayer coatings, which involve water-soluble polyelectrolytes without hydrophobic repeat units deposited from aqueous solutions.

In certain preferred embodiments, both of the copolymers may be of average molar mass of at least 30,000 g/mol, more preferably over 50,000 g/mol, and even more preferably of over 100,000 g/mol.

The two copolymers may be deposited onto the porous support to form a selective layer, for example, by one of the two following methods:

i) Sequential coating of each copolymer onto the support, creating at least one layer of anionic copolymer and one layer of cationic copolymer on the support. This family of membranes will be termed "bilayer membranes" below, though in principle a higher number of layers is also possible.
ii) Creating a mixture, or blend, of the two copolymers by dissolving both in the same solvent, then coating this blend onto the support, creating the selective layer. This family of membranes will be termed "blend membranes".

In each case, the support membrane's effective pore size is significantly higher than that of the TFC membrane; the selective layer significantly changes the rejection properties of the support.

Exemplary hydrophobic repeat units include repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA); other fluorinated acrylates, methacrylates, and acrylamides (*e.g.,* pentafluoropropyl methacrylate, heptafluorobutyl methacrylate,

pentafluorophenyl methacrylate); styrene; methyl methacrylate; acrylonitrile; 2-chloroethyl methacrylate; 2-bromoethyl methacrylate; allyl methacrylate; other monomers that fit the above criteria. Additionally, hydrophobic monomeric peptides or blocked amino acids with no ionizable/charged groups under use conditions can be used as the hydrophobic monomer unit.

Exemplary anionic repeat units include repeat units derived from methacrylic acid (MAA); 2-sulfoethyl methacrylate (SEMA); L-tryptophan-methacrylamide; D-tryptophan-methacrylamide; L or D-tryptophan-acrylamide; L or D-alanine-methacrylamide; L or D-alanine-acrylamide; L or D-valine-methacrylamide; L or D-valine-acrylamide; L or D-isoleucine-methacrylamide; L or D-isoleucine-acrylamide; L or D-allo-isoleucine-methacrylamide; L or D-allo-isoleucine-acrylamide; L or D-methionine-methacrylamide; L or D-methionine-acrylamide; L or D-phenylalanine-methacrylamide; L or D-phenylalanine-acrylamide; L or D-tyrosine-methacrylamide; L or D-tyrosine-acrylamide; L or D-histadine-methacrylamide; L or D-histadine-acrylamide; L or D-glutamic acid-methacrylamide; L or D-glutamic acid-methacrylamide; L or D-aspartic acid-acrylamide; L or D-aspartic acid-methacrylamide; acrylic acid; 2-carboxyethyl acrylate; mono-2-(methacryloyloxy)ethyl succinate; mono-2-(methacryloyloxy)ethyl maleate; sodium 4-vinylbenzenesulfonate; 2-acrylamido-2- methylpropane sulfonic acid; 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt; 2-acrylamido-2-methyl-1-propanesulfonic acid; 3-sulfopropyl acrylate potassium salt; 3-sulfopropyl methacrylate potassium salt; 3-vinylbenzoic acid; 4-vinylbenzoic acid; 2-vinylbenzoic acid; 4-(2- propenyl)benzoic acid; 2-methyl-2-propene-1-sulfonic acid sodium salt; vinylsulfonic acid sodium salt; vinylphosphonic acid; (4-ethenylphenyl)methylphosphonic acid; methacrylate, acrylate, methacrylamide, acrylamide, styrene, or vinyl derivatives containing carboxylic acid, sulfonate, phosphate, or other ionizable/charged groups that carry a negative charge under use conditions. As well as monomeric peptides with ionizable/charged groups that carry a negative charge under use conditions can be used as the anionic monomer unit.

Exemplary cationic repeat units include repeat units derived from [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MAETA); [3 (methacryloylamino)propyl] trimethylammonium chloride; [2-(acryloyloxy)ethyl] trimethylammonium chloride; (3-acrylamidopropyl)trimethylammonium chloride; 4-vinylbenzyl(triphenyl)phosphonium chloride; (vinylbenzyl)trimethylammonium chloridemethacrylate; 3-vinylaniline; 4-vinylaniline; 2-isopropenylaniline; N-(3-aminopropyl)methacrylamide hydrochloride; N-vinylimidazolium salts; 1-allyl-3-vinylimidazolium salts; 1-allyl-2methyl-5-vinyl-pyridinium salt; 1-allyl-5-vinyl-pyridinium

salt; 1-Methyl-1-(1-vinylcyclohexyl)pyrrolidinium iodide; methacrylate, acrylate, methacrylamide, acrylamide, styrene, or vinyl derivatives containing amine, pyridinium, imidazolium, phosphonium, pyrrolidinium, or other ionizable/charged groups that carry a positive charge under use conditions. Repeat units that have strong cationic charges (*e.g.*, quaternary amine groups) are preferred. Additionally, monomeric peptides with ionizable/charged groups that carry a positive charge under use conditions can be used as the cationic monomer unit.

In certain embodiments, the membranes described herein comprise the following features:

i) Lower effective pore size than the support

ii) Scalable manufacturing

In certain embodiments, the membranes disclosed herein, such as the bilayer membranes, comprise the following features:

- They exhibit lower effective pore size than membranes prepared by coating either just the anionic copolymer or just the cationic copolymer on the same support, quantified through measuring the rejection of a neutral solute.
- Their water permeances are within the range for commercial membranes of comparable effective pore size and can potentially tuned to be higher.
- Copolymers featuring essentially any pair of ionizable or charged groups (i.e., anionic and cationic) can be used to prepare them as long as they can be dissolved and coated. This is different from the blend membranes, where certain pairs of functional groups have very limited solubility and coagulate when mixed in solution, limiting available options.
- Without wishing to be bound by theory, it is believed that the selectivity of these membranes arises from a very thin layer at the interface of the two coated layers where the anionic and cationic copolymers interact and create a tighter "mesh" than each copolymer has in isolation.
- The selectivity/effective pore size of these membranes can be controlled by the hydrophobic/charged monomer ratio of each copolymer. Furthermore, the degree of interlayer mixing, which is affected by factors such as solvent choice, temperature, casting speed, external air flow, and post-processing may influence effective pore size, as well as the chemical nature of the pair of charged groups.
- These membranes show improved fouling resistant properties. For example, layers that are fully mixed (i.e., roughly homogeneous throughout) or close to fully mixed and

close to neutrally charged to be particularly fouling resistant, mimicking the polyampholyte membranes that have been reported before.

In addition, it is expected that the bilayer membranes can be designed to be cross-linkable, including at the interface (*e.g.,* via a reaction between the anionic copolymer and the cationic copolymer), further offering stability and tunability. These reactions could include reactions between, for example, epoxide with primary amine or alcohol; alkyl halide with tertiary amine; azide with alkyne. This would require either the presence of a third monomer unit in the polymers; and/or a reactive group either in the charged monomer units and/or hydrophobic monomer units.

In certain embodiments, the membranes disclosed herein, such as the blend membranes, comprise the following features:

- Blend membranes also have a lower effective pore size than the support, and usually than each separate copolymer, quantified through measuring the rejection of a neutral solute. Their effective pore sizes, however, are typically higher than membranes prepared using the bilayer approach with the same copolymers.
- Exhibit a highly tunable effective pore size, which can be controlled by changing the molar ratio of the anionic and cationic groups. This parameter can also control/change the permeance, and the salt rejection.
- Fouling-resistant, as compared with other membranes in the market, and those that are neutrally charged or close to neutrally charged will be particularly highly fouling resistant.

In certain embodiments, the membranes disclosed herein, such as the bilayer and blend membranes, comprise the following features

- Easy, scalable copolymer synthesis.
- Easy, scalable manufacturing of membranes using a broad and controlled range of selectivity, tunable for desired performance (*e.g.,* salt rejection, softening, size-based separation of organic molecules, water treatment for selective removal of contaminants).
- Fouling resistance to a range of foulants.
- Chlorine resistance.
- Chemical resistance.

In certain aspects, a material system and a method of manufacturing membranes are described that have improved capabilities. Past multilayer membranes incorporating charged groups have exclusively focused on water-soluble polyelectrolyte multi-layers, deposited by

adsorption from water; this invention describes rod-coating water-insoluble copolymers from organic solutions. The performance of the membranes is highly tunable and adaptable.

The membranes disclosed herein act differently than polyelectrolyte multi-layer membranes. The formation of a tightly interwoven/complexed layer at the interface of two separately deposited layers has not been reported in any other systems.

The disclosed invention can be used in many filtration processes where size- and charge-selective separations are needed, including water and wastewater treatment, and nutrient separation and recovery.

In one aspect, the present disclosure provides a composite membrane, comprising a porous support; and a selective layer comprising a first copolymer and a second copolymer; wherein:

the first copolymer comprises a first plurality of hydrophobic repeat units and a plurality of cationic repeat units;

the second copolymer comprises a second plurality of hydrophobic repeat units and a plurality of anionic repeat units; and

the first copolymer and the second copolymer are essentially insoluble in water (*e.g.,* under operating conditions).

In certain preferred embodiments, the first copolymer and the second copolymer are insoluble in water (*e.g.,* under operating conditions).

In certain embodiments, the composite membrane is a thin film composite membrane.

In certain embodiments, the composite membrane has a thickness of about 20 μm to about 1,000 μm. In certain embodiments, the composite membrane has a thickness of about 50 μm to about 200 μm.

In certain embodiments, the selective layer has a thickness of about 30 nm to about 5 μm. In certain embodiments, the selective layer has a thickness of about 30 nm to about 1,000 nm. In certain embodiments, the selective layer has a thickness of about 10 nm, about 25 nm, about 50 nm, about 75 nm, about 100 nm, about 125 nm, about 150 nm, about 175 nm, about 200 nm, about 225 nm, about 250 nm, about 275 nm, about 300 nm, about 325 nm, about 350 nm, about 375 nm, about 400 nm, about 425 nm, about 450 nm, about 475 nm, about 500 nm, about 525 nm, about 550 nm, about 575 nm, or about 600 nm. In certain embodiments, the selective layer has a thickness of about 400 nm, about 425 nm, about 450 nm, about 475 nm, about 500 nm, about 525 nm, about 550 nm, about 575 nm, or about 600 nm.

In certain embodiments, the plurality of cationic repeat units is partially positively charged in water (*e.g.,* in water at a neutral pH or in water under operating conditions). In

certain embodiments, the plurality of cationic repeat units is positively charged in water (*e.g.*, in water at a neutral pH or in water under operating conditions).

In certain embodiments, the plurality of anionic repeat units is partially negatively charged in water (*e.g.*, in water at a neutral pH or in water under operating conditions). In certain embodiments, the plurality of anionic repeat units is negatively charged in water (*e.g.*, in water at a neutral pH or in water under operating conditions).

In certain embodiments, the selective layer consists essentially of the first copolymer and a second copolymer.

In certain embodiments, the first copolymer comprises about 5 – 80 wt% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 15 – 75 wt% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 30 – 60 wt% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 10 wt%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 5 – 80 mol% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 15 – 75 mol% of the plurality of cationic repeat units.

In certain embodiments, the first copolymer comprises about 5 – 80 mol% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 15 – 75 mol% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 30 – 60 mol% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 10 mol%, about 20 mol%, about 30 mol%, about 40 mol%, about 50 mol%, about 60 mol%, about 70 mol%, or about 80 mol% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 5 – 80 mol% of the plurality of cationic repeat units. In certain embodiments, the first copolymer comprises about 15 – 75 mol% of the plurality of cationic repeat units.

In certain embodiments, the first copolymer comprises about 5 – 80 wt% of the plurality of the first plurality of hydrophobic repeat units. In certain embodiments, the first copolymer comprises about 15 – 75 wt% of the plurality of the first plurality of hydrophobic repeat units. In certain embodiments, the first copolymer comprises about 30 – 60 wt% of the plurality of the first plurality of hydrophobic repeat units. In certain embodiments, the first copolymer comprises about 10 wt%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the plurality of the first plurality of hydrophobic repeat units. In certain embodiments, the first copolymer comprises about 5 – 80 wt% of the

plurality of the first plurality of hydrophobic repeat units. In certain embodiments, the first copolymer comprises about 15 – 75 wt% of the plurality of the first plurality of hydrophobic repeat units.

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In certain embodiments, the second copolymer comprises about 5 – 80 wt% of the plurality of anionic repeat units. In certain embodiments, the second copolymer comprises about 15 – 75 wt% of the plurality of anionic repeat units. In certain embodiments, the second copolymer comprises about 30 – 60 wt% of the plurality of anionic repeat units. In certain embodiments, the second copolymer comprises about 10 wt%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the plurality of anionic repeat units. In certain embodiments, the second copolymer comprises about 5 – 80 mol% of the plurality of anionic repeat units. In certain embodiments, the second copolymer comprises about 15 – 75 mol% of the plurality of anionic repeat units.

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In certain embodiments, the first copolymer has an average molar mass of at least 50,000 g/mol. In certain embodiments, the first copolymer has an average molar mass of at least 100,000 g/mol. In certain embodiments, the first copolymer has an average molar mass of 20,000 g/mol to about 500,000 g/mol. In certain embodiments, the first copolymer has an average molar mass of 30,000 g/mol to about 500,000 g/mol. In certain embodiments, the first copolymer has an average molar mass of 50,000 g/mol to about 500,000 g/mol. In certain embodiments, the first copolymer has an average molar mass of 100,000 g/mol to about 500,000 g/mol.

In certain embodiments, the second copolymer has an average molar mass of at least 50,000 g/mol. In certain embodiments, the second copolymer has an average molar mass of at least 100,000 g/mol. In certain embodiments, the second copolymer has an average molar mass of 20,000 g/mol to about 500,000 g/mol. In certain embodiments, the second copolymer has an average molar mass of 30,000 g/mol to about 500,000 g/mol. In certain embodiments, the second copolymer has an average molar mass of 50,000 g/mol to about 500,000 g/mol. In

certain embodiments, the second copolymer has an average molar mass of 100,000 g/mol to about 500,000 g/mol.

In certain embodiments, the first copolymer and the second copolymer are sequentially layered on the porous support (*e.g.*, the first copolymer and the second copolymer have been applied to the porous support layer sequentially). In certain embodiments, the first copolymer is the first layer (*e.g.*, the outermost layer) and the second copolymer is the second layer (*e.g.*, the first copolymer layer is on the second copolymer layer and the second copolymer layer is in contact with the porous support). In other embodiments, the second copolymer is the first layer (*e.g.*, the outmost layer) and the first copolymer is the second layer (*e.g.*, the second copolymer layer is on the first copolymer layer and the first copolymer layer is in contact with the porous support). In other embodiments, the first copolymer and the second copolymer are intermingled on the porous support (*e.g.*, the first copolymer and the second copolymer form a homogenous layer on the porous support).

In certain embodiments, the first plurality of hydrophobic repeat units comprises repeat units derived from acrylates (*e.g.*, alkyl acrylates, fluorinated acrylates or methacrylates), acrylamides (*e.g.*, fluorinated acrylamides), styrene, or hydrophobic amino acids. In certain embodiments, the first plurality of hydrophobic repeat units comprises repeat units derived from methacrylate. In certain embodiments, the first plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA), pentafluoropropyl methacrylate, heptafluorobutyl, pentafluorophenyl methacrylate, styrene, methyl methacrylate, acrylonitrile, 2-chloroethyl methacrylate, 2-bromoethyl methacrylate, and allyl methacrylate. In certain preferred embodiments, the first plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA).

In certain embodiments, the second plurality of hydrophobic repeat units comprises repeat units derived from acrylates (*e.g.*, alkyl acrylates, fluorinated acrylates or methacrylates), acrylamides (*e.g.*, fluorinated acrylamides), styrene, or hydrophobic amino acids. In certain embodiments, the second plurality of hydrophobic repeat units comprises repeat units derived from methacrylate. In certain embodiments, the second plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA), pentafluoropropyl methacrylate, heptafluorobutyl, pentafluorophenyl methacrylate, styrene, methyl methacrylate, acrylonitrile, 2-chloroethyl methacrylate, 2-bromoethyl methacrylate, and allyl methacrylate. In certain preferred embodiments, the second plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA).

In certain embodiments, the plurality of cationic repeat units comprises repeat units derived from acrylate, acrylamide, styrene, or vinyl monomers substituted with amine, pyridinium, imidazolium, phosphonium, or pyrrolidinium. In certain embodiments, the plurality of cationic repeat units comprises repeat units derived from [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MAETA), [3 (methacryloylamino)propyl] trimethylammonium chloride, [2-(acryloyloxy)ethyl] trimethylammonium chloride, (3-acrylamidopropyl)trimethylammonium chloride; 4-vinylbenzyl(triphenyl)phosphonium chloride, (vinylbenzyl)trimethylammonium chloridemethacrylate, 3-vinylaniline, 4-vinylaniline, 2-isopropenylaniline, N-(3-aminopropyl)methacrylamide hydrochloride, N-vinylimidazolium, 1-allyl-3-vinylimidazoliums, 1-allyl-2methyl-5-vinyl-pyridinium, 1-allyl-5-vinyl-pyridinium, or 1-Methyl-1-(1-vinylcyclohexyl)pyrrolidinium iodide. In certain preferred embodiments, the plurality of cationic repeat units comprises repeat units derived from 2-(methacryloyloxy)ethyl]trimethylammonium chloride.

In certain embodiments, the plurality of anionic repeat units comprises repeat units derived from acrylate, acrylamide, styrene, or vinyl monomers substituted with carboxylic acid, sulfonate, or phosphate. In certain embodiments, the plurality of anionic repeat units comprises repeat units derived from methacrylate. In certain embodiments, the plurality of anionic repeat units comprises repeat units derived from methacrylic acid (MAA), 2-sulfoethyl methacrylate (SEMA), L-tryptophan-methacrylamide, D-tryptophan-methacrylamide, L or D-tryptophan-acrylamide, L or D-alanine-methacrylamide, L or D-alanine-acrylamide, L or D-valine-methacrylamide, L or D-valine-acrylamide, L or D-isoleucine-methacrylamide, L or D-isoleucine-acrylamide, L or D-allo-isoleucine-methacrylamide, L or D-allo-isoleucine-acrylamide, L or D-methionine-methacrylamide, L or D-methionine-acrylamide, L or D-phenylalanine-methacrylamide, L or D-phenylalanine-acrylamide, L or D-tyrosine-methacrylamide, L or D-tyrosine-acrylamide, L or D-histadine-methacrylamide, L or D-histadine-acrylamide, L or D-glutamic acid-methacrylamide, L or D-glutamic acid-methacrylamide, L or D-aspartic acid-acrylamide, L or D-aspartic acid-methacrylamide, acrylic acid, 2-carboxyethyl acrylate, mono-2-(methacryloyloxy)ethyl succinate, mono-2-(methacryloyloxy)ethyl maleate, sodium 4-vinylbenzenesulfonate, 2-acrylamido-2-methylpropane sulfonic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt, 2-acrylamido-2-methyl-1-propanesulfonic acid, 3-sulfopropyl acrylate potassium salt, 3-sulfopropyl methacrylate potassium salt, 3-vinylbenzoic acid, 4-vinylbenzoic acid, 2-vinylbenzoic acid, 4-(2- propenyl)benzoic acid, 2-methyl-2-propene-1-sulfonic acid sodium

salt, vinylsulfonic acid sodium salt, vinylphosphonic acid, or (4-ethenylphenyl)methylphosphonic acid. In certain preferred embodiments, the plurality of anionic repeat units comprises repeat units derived from 2-sulfoethyl methacrylate. In other preferred embodiments, the plurality of anionic repeat units comprises repeat units derived from methacrylic acid.

In certain embodiments, the first copolymer is a block copolymer. In certain embodiments, the first copolymer is a statistical (*e.g.,* approximately random) copolymer. In certain preferred embodiments, the first copolymer is a random copolymer. In certain embodiments, the second copolymer is a graft copolymer or a comb-shaped copolymer.

In certain embodiments, the second copolymer is a block copolymer. In certain embodiments, the first copolymer is a statistical (*e.g.,* approximately random) copolymer. In certain preferred embodiments, the second copolymer is a random copolymer. In certain preferred embodiments, the second copolymer is a graft copolymer or a comb-shaped copolymer.

In certain embodiments, the effective pore size of the composite membrane is less than the effective pore size of a membrane prepared by coating only the first copolymer or only the second copolymer on the same porous support. In certain embodiments, the effective pore size is quantified by measuring the rejection of a neutral (*e.g.,* uncharged) solute.

In certain embodiments, the first copolymer is crosslinked.

In certain embodiments, the second copolymer is crosslinked.

In another aspect, the present disclosure provides methods of separating a solute from a solution, comprising contacting the solution with a composite membrane. In certain embodiments, the solution is passed (*e.g.,* filtered) through the composite membrane. In certain embodiments, the solute is a salt (*e.g.,* sodium chloride). In certain embodiments, the solution is seawater.

In another aspect, the present disclosure provides methods of fabricating a composite membrane disclosed herein comprising applying a first copolymer, as disclosed herein, and a second copolymer, as disclosed herein, to a porous support, thereby fabricating a composite membrane disclosed herein.

In certain embodiments, the first copolymer and the second copolymer are applied to the porous support layer sequentially, thereby forming a bilayer membrane. In certain embodiments, the first copolymer is applied first, and the second copolymer is applied second. In certain embodiments, the first copolymer is applied second, and the second copolymer is applied first. In other embodiments, the first copolymer and the second copolymer are applied

to the porous support layer as a blend (*e.g.*, the first copolymer and second copolymer are mixed before application), thereby forming a blend membrane.

In certain embodiments, the first copolymer is dissolved in a protic solvent (*e.g.*, methanol) prior to application. In certain embodiments, the second copolymer is dissolved in a protic solvent (*e.g.*, methanol) prior to application. In certain embodiments, the first copolymer and the second copolymer are each dissolved in a protic solvent (*e.g.*, methanol) prior to application.

Definitions

Unless otherwise defined herein, scientific and technical terms used in this application shall have the meanings that are commonly understood by those of ordinary skill in the art.

The methods and techniques of the present disclosure are generally performed, unless otherwise indicated, according to conventional methods well known in the art and as described in various general and more specific references that are cited and discussed throughout this specification.

Chemistry terms used herein, unless otherwise defined herein, are used according to conventional usage in the art, as exemplified by "The McGraw-Hill Dictionary of Chemical Terms", Parker S., Ed., McGraw-Hill, San Francisco, C.A. (1985).

All of the above, and any other publications, patents and published patent applications referred to in this application are specifically incorporated by reference herein. In case of conflict, the present specification, including its specific definitions, will control.

As used herein, the terms "optional" or "optionally" mean that the subsequently described event or circumstance may occur or may not occur, and that the description includes instances where the event or circumstance occurs as well as instances in which it does not. For example, "optionally substituted alkyl" refers to the alkyl may be substituted as well as where the alkyl is not substituted.

It is understood that substituents and substitution patterns on the compounds of the present invention can be selected by one of ordinary skilled person in the art to result chemically stable compounds which can be readily synthesized by techniques known in the art, as well as those methods set forth below, from readily available starting materials. If a substituent is itself substituted with more than one group, it is understood that these multiple groups may be on the same carbon or on different carbons, so long as a stable structure results.

As used herein, the term "optionally substituted" refers to the replacement of one to six hydrogen radicals in a given structure with the radical of a specified substituent including, but

not limited to: hydroxyl, hydroxyalkyl, alkoxy, halogen, alkyl, nitro, silyl, acyl, acyloxy, aryl, cycloalkyl, heterocyclyl, amino, aminoalkyl, cyano, haloalkyl, haloalkoxy, -OCO-CH_2-O-alkyl, -OP(O)(O-alkyl)$_2$ or –CH_2-OP(O)(O-alkyl)$_2$. Preferably, "optionally substituted" refers to the replacement of one to four hydrogen radicals in a given structure with the substituents mentioned above. More preferably, one to three hydrogen radicals are replaced by the substituents as mentioned above. It is understood that the substituent can be further substituted.

As used herein, the term "alkyl" refers to saturated aliphatic groups, including but not limited to C_1-C_{10} straight-chain alkyl groups or C_1-C_{10} branched-chain alkyl groups. Preferably, the "alkyl" group refers to C_1-C_6 straight-chain alkyl groups or C_1-C_6 branched-chain alkyl groups. Most preferably, the "alkyl" group refers to C_1-C_4 straight-chain alkyl groups or C_1-C_4 branched-chain alkyl groups. Examples of "alkyl" include, but are not limited to, methyl, ethyl, 1-propyl, 2-propyl, n-butyl, sec-butyl, tert-butyl, 1-pentyl, 2-pentyl, 3-pentyl, neo-pentyl, 1-hexyl, 2-hexyl, 3-hexyl, 1-heptyl, 2-heptyl, 3-heptyl, 4-heptyl, 1-octyl, 2-octyl, 3-octyl or 4-octyl and the like. The "alkyl" group may be optionally substituted.

The term "acyl" is art-recognized and refers to a group represented by the general formula hydrocarbylC(O)-, preferably alkylC(O)-.

The term "acylamino" is art-recognized and refers to an amino group substituted with an acyl group and may be represented, for example, by the formula hydrocarbylC(O)NH-.

The term "acyloxy" is art-recognized and refers to a group represented by the general formula hydrocarbylC(O)O-, preferably alkylC(O)O-.

The term "alkoxy" refers to an alkyl group having an oxygen attached thereto. Representative alkoxy groups include methoxy, ethoxy, propoxy, tert-butoxy and the like.

The term "alkoxyalkyl" refers to an alkyl group substituted with an alkoxy group and may be represented by the general formula alkyl-O-alkyl.

The term "alkyl" refers to saturated aliphatic groups, including straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl-substituted cycloalkyl groups, and cycloalkyl-substituted alkyl groups. In preferred embodiments, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (*e.g.*, C_{1-30} for straight chains, C_{3-30} for branched chains), and more preferably 20 or fewer.

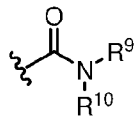
Moreover, the term "alkyl" as used throughout the specification, examples, and claims is intended to include both unsubstituted and substituted alkyl groups, the latter of which refers to alkyl moieties having substituents replacing a hydrogen on one or more carbons of the hydrocarbon backbone, including haloalkyl groups such as trifluoromethyl and 2,2,2-trifluoroethyl, etc.

The term "C_{x-y}" or "C_x-C_y", when used in conjunction with a chemical moiety, such as, acyl, acyloxy, alkyl, alkenyl, alkynyl, or alkoxy is meant to include groups that contain from x to y carbons in the chain. C_0alkyl indicates a hydrogen where the group is in a terminal position, a bond if internal. A C_{1-6}alkyl group, for example, contains from one to six carbon atoms in the chain.

The term "alkylamino", as used herein, refers to an amino group substituted with at least one alkyl group.

The term "alkylthio", as used herein, refers to a thiol group substituted with an alkyl group and may be represented by the general formula alkylS-.

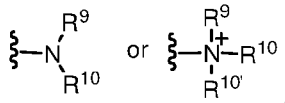
The term "amido", as used herein, refers to a group



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wherein R^9 and R^{10} each independently represent a hydrogen or hydrocarbyl group, or R^9 and R^{10} taken together with the N atom to which they are attached complete a heterocycle having from 4 to 8 atoms in the ring structure.

The terms "amine" and "amino" are art-recognized and refer to both unsubstituted and substituted amines and salts thereof, *e.g.*, a moiety that can be represented by



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wherein R^9, R^{10}, and $R^{10'}$ each independently represent a hydrogen or a hydrocarbyl group, or R^9 and R^{10} taken together with the N atom to which they are attached complete a heterocycle having from 4 to 8 atoms in the ring structure.

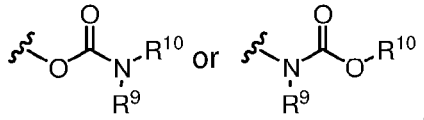
The term "aminoalkyl", as used herein, refers to an alkyl group substituted with an amino group.

The term "aralkyl", as used herein, refers to an alkyl group substituted with an aryl group.

The term "aryl" as used herein include substituted or unsubstituted single-ring aromatic groups in which each atom of the ring is carbon. Preferably the ring is a 5- to 7-membered ring, more preferably a 6-membered ring. The term "aryl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is aromatic, *e.g.*, the other cyclic rings can be cycloalkyls,

cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Aryl groups include benzene, naphthalene, phenanthrene, phenol, aniline, and the like.

The term "carbamate" is art-recognized and refers to a group



wherein R^9 and R^{10} independently represent hydrogen or a hydrocarbyl group.

The term "carbocyclylalkyl", as used herein, refers to an alkyl group substituted with a carbocycle group.

The term "carbocycle" includes 5-7 membered monocyclic and 8-12 membered bicyclic rings. Each ring of a bicyclic carbocycle may be selected from saturated, unsaturated and aromatic rings. Carbocycle includes bicyclic molecules in which one, two or three or more atoms are shared between the two rings. The term "fused carbocycle" refers to a bicyclic carbocycle in which each of the rings shares two adjacent atoms with the other ring. Each ring of a fused carbocycle may be selected from saturated, unsaturated and aromatic rings. In an exemplary embodiment, an aromatic ring, *e.g.,* phenyl, may be fused to a saturated or unsaturated ring, *e.g.,* cyclohexane, cyclopentane, or cyclohexene. Any combination of saturated, unsaturated and aromatic bicyclic rings, as valence permits, is included in the definition of carbocyclic. Exemplary "carbocycles" include cyclopentane, cyclohexane, bicyclo[2.2.1]heptane, 1,5-cyclooctadiene, 1,2,3,4-tetrahydronaphthalene, bicyclo[4.2.0]oct-3-ene, naphthalene and adamantane. Exemplary fused carbocycles include decalin, naphthalene, 1,2,3,4-tetrahydronaphthalene, bicyclo[4.2.0]octane, 4,5,6,7-tetrahydro-1H-indene and bicyclo[4.1.0]hept-3-ene. "Carbocycles" may be substituted at any one or more positions capable of bearing a hydrogen atom.

The term "carbocyclylalkyl", as used herein, refers to an alkyl group substituted with a carbocycle group.

The term "carbonate" is art-recognized and refers to a group $-OCO_2-$.

The term "carboxy", as used herein, refers to a group represented by the formula $-CO_2H$.

The term "cycloalkyl" includes substituted or unsubstituted non-aromatic single ring structures, preferably 4- to 8-membered rings, more preferably 4- to 6-membered rings. The term "cycloalkyl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is cycloalkyl and the substituent (*e.g.,* R^{100}) is attached to the cycloalkyl ring, *e.g.,* the other

cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Heteroaryl groups include, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrazine, pyridazine, pyrimidine, denzodioxane, tetrahydroquinoline, and the like.

The term "ester", as used herein, refers to a group $-C(O)OR^9$ wherein R^9 represents a hydrocarbyl group.

The term "ether", as used herein, refers to a hydrocarbyl group linked through an oxygen to another hydrocarbyl group. Accordingly, an ether substituent of a hydrocarbyl group may be hydrocarbyl-O-. Ethers may be either symmetrical or unsymmetrical. Examples of ethers include, but are not limited to, heterocycle-O-heterocycle and aryl-O-heterocycle. Ethers include "alkoxyalkyl" groups, which may be represented by the general formula alkyl-O-alkyl.

The terms "halo" and "halogen" as used herein means halogen and includes chloro, fluoro, bromo, and iodo.

The terms "hetaralkyl" and "heteroaralkyl", as used herein, refers to an alkyl group substituted with a hetaryl group.

The terms "heteroaryl" and "hetaryl" include substituted or unsubstituted aromatic single ring structures, preferably 5- to 7-membered rings, more preferably 5- to 6-membered rings, whose ring structures include at least one heteroatom, preferably one to four heteroatoms, more preferably one or two heteroatoms. The terms "heteroaryl" and "hetaryl" also include polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is heteroaromatic, *e.g.,* the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Heteroaryl groups include, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrazine, pyridazine, and pyrimidine, and the like.

The term "heteroatom" as used herein means an atom of any element other than carbon or hydrogen. Preferred heteroatoms are nitrogen, oxygen, and sulfur.

The term "heterocyclylalkyl", as used herein, refers to an alkyl group substituted with a heterocycle group.

The terms "heterocyclyl", "heterocycle", and "heterocyclic" refer to substituted or unsubstituted non-aromatic ring structures, preferably 3- to 10-membered rings, more preferably 3- to 7-membered rings, whose ring structures include at least one heteroatom, preferably one to four heteroatoms, more preferably one or two heteroatoms. The terms "heterocyclyl" and "heterocyclic" also include polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least

one of the rings is heterocyclic, *e.g.*, the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Heterocyclyl groups include, for example, piperidine, piperazine, pyrrolidine, morpholine, lactones, lactams, and the like.

The term "hydrocarbyl", as used herein, refers to a group that is bonded through a carbon atom that does not have a =O or =S substituent, and typically has at least one carbon-hydrogen bond and a primarily carbon backbone, but may optionally include heteroatoms. Thus, groups like methyl, ethoxyethyl, 2-pyridyl, and even trifluoromethyl are considered to be hydrocarbyl for the purposes of this application, but substituents such as acetyl (which has a =O substituent on the linking carbon) and ethoxy (which is linked through oxygen, not carbon) are not. Hydrocarbyl groups include, but are not limited to aryl, heteroaryl, carbocycle, heterocycle, alkyl, alkenyl, alkynyl, and combinations thereof.

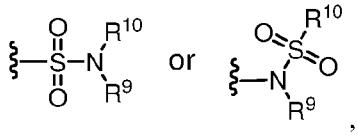
The term "hydroxyalkyl", as used herein, refers to an alkyl group substituted with a hydroxy group.

The term "lower" when used in conjunction with a chemical moiety, such as, acyl, acyloxy, alkyl, alkenyl, alkynyl, or alkoxy is meant to include groups where there are ten or fewer atoms in the substituent, preferably six or fewer. A "lower alkyl", for example, refers to an alkyl group that contains ten or fewer carbon atoms, preferably six or fewer. In certain embodiments, acyl, acyloxy, alkyl, alkenyl, alkynyl, or alkoxy substituents defined herein are respectively lower acyl, lower acyloxy, lower alkyl, lower alkenyl, lower alkynyl, or lower alkoxy, whether they appear alone or in combination with other substituents, such as in the recitations hydroxyalkyl and aralkyl (in which case, for example, the atoms within the aryl group are not counted when counting the carbon atoms in the alkyl substituent).

The terms "polycyclyl", "polycycle", and "polycyclic" refer to two or more rings (*e.g.*, cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls) in which two or more atoms are common to two adjoining rings, *e.g.*, the rings are "fused rings". Each of the rings of the polycycle can be substituted or unsubstituted. In certain embodiments, each ring of the polycycle contains from 3 to 10 atoms in the ring, preferably from 5 to 7.

The term "sulfate" is art-recognized and refers to the group $-OSO_3H$, or a pharmaceutically acceptable salt thereof.

The term "sulfonamido" is art-recognized and refers to the group represented by the general formulae



wherein R^9 and R^{10} independently represents hydrogen or hydrocarbyl.

The term "sulfoxide" is art-recognized and refers to the group –S(O)-.

The term "sulfonate" is art-recognized and refers to the group SO_3H, or a pharmaceutically acceptable salt thereof.

The term "sulfone" is art-recognized and refers to the group $–S(O)_2-$.

The term "substituted" refers to moieties having substituents replacing a hydrogen on one or more carbons of the backbone. It will be understood that "substitution" or "substituted with" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, *e.g.,* which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc. As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and non-aromatic substituents of organic compounds. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. Substituents can include any substituents described herein, for example, a halogen, a hydroxyl, a carbonyl (such as a carboxyl, an alkoxycarbonyl, a formyl, or an acyl), a thiocarbonyl (such as a thioester, a thioacetate, or a thioformate), an alkoxyl, a phosphoryl, a phosphate, a phosphonate, a phosphinate, an amino, an amido, an amidine, an imine, a cyano, a nitro, an azido, a sulfhydryl, an alkylthio, a sulfate, a sulfonate, a sulfamoyl, a sulfonamido, a sulfonyl, a heterocyclyl, an aralkyl, or an aromatic or heteroaromatic moiety. It will be understood by those skilled in the art that the moieties substituted on the hydrocarbon chain can themselves be substituted, if appropriate.

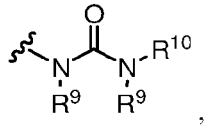
The term "thioalkyl", as used herein, refers to an alkyl group substituted with a thiol group.

The term "thioester", as used herein, refers to a group $-C(O)SR^9$ or $–SC(O)R^9$

wherein R^9 represents a hydrocarbyl.

The term "thioether", as used herein, is equivalent to an ether, wherein the oxygen is replaced with a sulfur.

The term "urea" is art-recognized and may be represented by the general formula



wherein R^9 and R^{10} independently represent hydrogen or a hydrocarbyl.

Many of the compounds useful in the methods and compositions of this disclosure have at least one stereogenic center in their structure. This stereogenic center may be present in a R or a S configuration, said R and S notation is used in correspondence with the rules described in Pure Appl. Chem. (1976), 45, 11-30. The disclosure contemplates all stereoisomeric forms such as enantiomeric and diastereoisomeric forms of the compounds, salts, prodrugs or mixtures thereof (including all possible mixtures of stereoisomers). See, *e.g.,* WO 01/062726.

Furthermore, certain compounds which contain alkenyl groups may exist as Z (zusammen) or E (entgegen) isomers. In each instance, the disclosure includes both mixture and separate individual isomers.

As used herein, the term "operating conditions" refers to the conditions under which a filtration membrane typically is used or operates. For example, in certain embodiments, a filtration membrane may be designed to treat produced water (*e.g.,* water that is produced as a byproduct during the extraction of oil and natural gas), grey water (*e.g.,* water that already has been used domestically, commercially and industrially), a hot stream (*e.g.,* frack water), a saline stream, water from mine drainage, or industrial cleaning. In certain embodiments, the term "operating conditions" may refer to conditions associated with the treatment of acidic water, optionally containing suspended solids (*e.g.,* inorganic salts). In other embodiments, the operating conditions may refer to conditions associated with the treatment of basic water, optionally containing suspended solids (*e.g.,* inorganic salts).

EXAMPLES

The invention now being generally described, it will be more readily understood by reference to the following examples which are included merely for purposes of illustration of certain aspects and embodiments of the present invention and are not intended to limit the invention.

Example 1

Synthesis and membrane preparation of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl

methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

Synthesis of **A+** (P(TFEMA-*r*-MAETA)). MAETA (4.00g, 19.3 mmol), and TFEMA (4.00g, 23.8 mmol) were dissolved in this order in DMSO (32 mL). AIBN (0.008g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 60° C, while stirring at 300 rpm for 17 hours. The flask was removed from the oil bath and unsealed, and 0.8 g of MEHQ was added to terminate the reaction. The reaction mixture was then precipitated in acetone and purified by stirring two fresh portions of 1:3 ethanol to hexane volume ratio for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72h at 60 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 1), using the ratio of protons from the two different monomer units. The calculated composition was: 41 mol% MAETA, and 59 mol% TFEMA. The final conversion of this reaction was 45%.

Synthesis of **S-** (P(TFEMA-*r*-SEMA)). SEMA (4.00g, 20.6 mmol), and TFEMA (4.00g, 23.8 mmol) were dissolved in this order in DMSO (32 mL). AIBN (0.008g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 60° C, while stirring at 300 rpm for 17 hours. The flask was removed from the oil bath and unsealed, and 0.8 g of MEHQ was added to terminate the reaction. The reaction mixture was then precipitated in 1:3 ethanol to hexane volume ratio and purified by stirring two fresh portions of 2:3 ethanol to hexane volume ratio for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72h at 60 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 2), using the ratio of protons from the two different monomer units. The calculated composition was: 37 mol% SEMA, and 63 mol% TFEMA. The final conversion of this reaction was 55%.

After both syntheses, thin film composite membranes were prepared using both copolymers A+ and S-. Each copolymer (0.5 g) was dissolved separately in methanol (9.5 g) at approximately 25° C. Both copolymer solutions were passed through 0.45 micrometer syringe filters (Whatman) and degassed in a vacuum oven for at least 1 hour. The membranes were prepared by coating a thin layer of each copolymer solution at a time on top of a commercial ultrafiltration (UF) membrane using a film applicator rod, additionally, in between coatings, a 10 min solvent evaporation period was adopted. When S- was coated first the membranes were named **SA**, and when A+ was coated first the membranes were named **AS**.

PS35 (**PSf**) ultrafiltration membrane, purchased from Solecta (Oceanside, Calif.), was used as the base membrane. After coating, the membrane was immersed in a water bath.

Additionally, coatings comprising less concentrated top layer solutions were tested. **SA** and **AS** stand for both solutions at 5 wt%, as described above. **SA1** and **AS1** stand for the first casting solution at 5 wt% and the second one at 1 wt%. **SA0.2** and **AS0.2** stand for the first casting solution at 5 wt% and the second one at 0.2 wt%. Membranes with only one layer as controls, **S-** and **A+** were also made

Film thickness and morphology was determined by the examination of freeze-fractured cross-sections of the membranes using a scanning electron microscope. The coating layer can be observed with a thickness of about 0.6 micrometers. FIG. 3.

Example 2

Water permeance and uptake of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the pure water fluxes through the membranes described in example 1 were measured using an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. After a stabilization period of at least one hour, a sample of the permeate was collected over 120 minutes and weighed. The value obtained was divided by filtration area and experiment time to obtain flux. The flux value was normalized by pressure to obtain pure water permeance (Table 1, 2, and 3). These membranes have permeances comparable to nanofiltration and ultrafiltration commercial membranes.

Table 1. Water permeance of controls and both APEC multilayers SA and SA.

	S-	SA	AS	A+
Permeance ($L/(m^2.h.bar)$)	4 ± 1	3 ± 1	20 ± 5	82 ± 16

Table 2. Water permeance of control and all layers with S- as the first layer.

	S-	SA0.2	SA1	SA
Permeance ($L/(m^2.h.bar)$)	4.0 ± 1.3	3.8 ± 1.3	3.2 ± 1.0	3.1 ± 1.1

Table 3. Water permeance of control and all layers with A+ as the first layer.

	A+	AS0.2	AS1	AS
Permeance (L/(m^2.h.bar))	82 ± 16	28 ± 7	21 ± 6	20 ± 5

Water uptake measurements (Table 4) were performed by utilizing approximately 40 micrometers thick polymer films. The films were prepared by mixing equal amounts (by weight) of S- and A+ copolymer solutions (both 5 wt%) on a Teflon dish, the mixture was left overnight to dry on a nutating mixer. The films were equilibrated in deionized water at room temperature overnight, excess water was removed by placing the films onto a Kimwipe for 5 s, after that the samples were weighted. The dry weight was obtained from drying the same samples overnight in a vacuum oven set at 60 °C.

Table 4. Water uptake of controls and APEC.

	S-	SA	A+
Water uptake (%)	285 ± 15	69 ± 8	1450 ± 310

Example 3

Neutral solute rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membranes prepared as described in example 1 were used in experiments aimed at identifying their effective pore size, or size cut-off. Dye molecules and sugars were used to probe this property. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a 0.1 mM solution of the probe dye (vitamin B12 (B12), or riboflavin (Rib)); or 4000 ppm solution of sugar molecule (sucrose, or glucose) or glycerol in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by COD kits (K-7365, CHEMetrics), or UV–vis spectrometer (Genesys10, ThermoScientific) and the solute rejection (%) was calculated (FIG.s 4, and 5). The cell was

rinsed several times with water. Pure water was filtered through the membrane until the permeate was completely clear before switching to a new solute.

Example 4

Salt rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membranes prepared as described in example 1 were used in experiments to determine their salt retention properties. Different salts at different concentrations were used to probe this property, their concentrations were easily measured by a standard conductivity probe. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a solution of the probe salt in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by the conductivity probe and the salt rejection (%) was calculated (FIG.s 6-14). The cell was rinsed several times with water. Pure water was filtered through the membrane until the permeate volume reaches 1 mL before switching to a new salt solution.

Example 5

Fouling resistance of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, two membranes, S- and SA, prepared as described in example 1 were used in experiments to determine their fouling resistance properties. The experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm2. The cell was stirred at 500 rpm. The feed solution consisted of a 1500 ppm oil-in-water emulsion (9:1 ratio of soybean oil:DC 193 surfactant obtained from Dow-Corning), prepared by blending the oil, water, and surfactant using a blender in high rpm for 3 min.

Example 6

Synthesis and membrane preparation of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl

methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

A+ was synthesized using the same protocol of example 1 and same copolymer (FIG. 1) was used.

Synthesis of **M-** (P(TFEMA-*r*-MAA)). MAA (10.00g), and TFEMA (10.00g) were dissolved in this order in DMSO (100 mL). AIBN (0.02g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 55° C, while stirring at 300 rpm for 4 hours. The flask was removed from the oil bath and unsealed, and 2 g of MEHQ in 10 mL of DMSO was added to terminate the reaction. The reaction mixture was then precipitated in 1:3 ethanol to hexane volume ratio and purified by stirring two fresh portions of 1:3 ethanol to hexane volume ratio for at least 8 hours. Finally, the copolymer was dried in the vacuum oven for 120h at 50 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 16), using the ratio of protons from the two different monomer units. The calculated composition was: 59 mol% MAA, and 41 mol% TFEMA. The final conversion of this reaction was 35%.

After both syntheses, thin film composite membranes were prepared using both copolymers A+ and M-. Each copolymer (0.5 g) was dissolved separately in methanol (9.5 g) at approximately 25° C. Both copolymer solutions were passed through 0.45 micrometer syringe filters (Whatman) and degassed in a vacuum oven for at least 1 hour. The membranes were prepared by coating a thin layer of each copolymer solution at a time on top of a commercial ultrafiltration (UF) membrane using a film applicator rod, additionally, in between coatings a 10 min solvent evaporation period was adopted. When M- was coated first the membrane was named **MA**, and when A+ was coated first the membrane was named **AM**. PS35 (**PSf**) ultrafiltration membrane, purchased from Solecta (Oceanside, Calif.), was used as the base membrane. After coating, the membrane was immersed in a water bath.

Film thickness and morphology was determined by the examination of freeze-fractured cross-sections of the membranes using a scanning electron microscope. The coating layer can be observed with a thickness of about 0.4 micrometers. FIG. 17.

Example 7

Water permeance of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the pure water flux through the membrane described in example 6, AM, was measured using an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. After a stabilization period of at least one hour, a sample of the permeate was collected over 120 minutes and weighed. The value obtained was divided by filtration area and experiment time to obtain flux. The flux value was normalized by pressure to obtain a pure water permeance of 1.5 L/m^2.h.bar.

Example 8

Neutral solute rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membrane prepared as described in example 6 was used in experiments aimed at identifying their effective pore size, or size cut-off. Vitamin B12 was used to probe this property. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a 0.1 mM solution of the probe dye (vitamin B12 (B12)) in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by UV–vis spectrometer (Genesys10, ThermoScientific) and the solute rejection was calculated to be 95.3%.

Example 9

Synthesis and membrane preparation of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) blends

A+ and **M-** were synthesized using the same protocols of Examples 1 and 6, and the same copolymers (FIG.s 1 and 16 respectively) were used.

After both syntheses, thin film composite membranes were prepared using both copolymers A+ and M-. Each copolymer (0.5 g) was dissolved separately in methanol (9.5 g)

at approximately 25° C. Both solutions were combined into solutions with different molar ratios of the ionizable/charged monomeric units and passed all solutions through a 0.45 micrometer syringe filter (Whatman) and degassed them in a vacuum oven for at least 1 hour. The membranes were prepared by coating a thin layer of the combined solutions on top of a commercial ultrafiltration (UF) membrane using a film applicator rod. PS35 (**PSf**) ultrafiltration membrane, purchased from Solecta (Oceanside, Calif.), was used as the base membrane. After coating, the membranes were immersed in a water bath.

Film thickness and morphology was determined by the examination of freeze-fractured cross-sections of the membranes using a scanning electron microscope. The coating layer can be observed with a thickness of about 3 micrometers. FIG. 18.

Example 10
Water permeance of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) blends

In this example, the pure water fluxes through the membranes described in example 9 were measured using an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. After a stabilization period of at least one hour, a sample of the permeate was collected over 120 minutes and weighed. The value obtained was divided by filtration area and experiment time to obtain flux. The flux value was normalized by pressure to obtain pure water permeance (FIG. 19). These membranes have permeances comparable to nanofiltration and ultrafiltration commercial membranes.

Example 11
Neutral solute rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) blends

In this example, the membrane prepared as described in example 9 were used in experiments aimed at identifying their effective pore size, or size cut-off. Vitamin B12 was used to probe this property. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a 0.1 mM

solution of the probe dye (vitamin B12 (B12)) in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by UV–vis spectrometer (Genesys10, ThermoScientific) and the solute rejection was calculated (FIG. 20).

Example 12
Salt rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (methacrylic acid) (M-) used as an Amphiphilic Polyelectrolyte Complex (APEC) blends

In this example, the membranes prepared as described in example 9 were used in experiments to determine their salt retention properties. Different salts at different concentrations were used to probe this property, their concentrations were easily measured by a standard conductivity probe. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a solution of the probe salt in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by the conductivity probe and the salt rejection (%) was calculated (FIG. 21-23). The cell was rinsed several times with water. Pure water was filtered through the membrane until the permeate volume reaches 1 mL before switching to a new salt solution.

Example 13
Synthesis and membrane preparation of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A2+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) is synthesized using a higher content of TFEMA (**A2+**). While the anionic copolymer is the same S- copolymer described in example 1.

Synthesis of **A2+** (P(TFEMA-*r*-MAETA)). MAETA (3.50g), and TFEMA (6.50g) were dissolved in this order in DMSO (40 mL). AIBN (0.01g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 60° C, while stirring at 300

rpm for 17 hours. The flask was removed from the oil bath and unsealed, and 1.0 g of MEHQ was added to terminate the reaction. The reaction mixture was then precipitated in acetone and purified by stirring two fresh portions of acetone for at least 3 hours, then two fresh portions of DI water for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72h at 60 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 24), using the ratio of protons from the two different monomer units. The calculated composition was: 34 wt% MAETA, and 66 wt% TFEMA. The final conversion of this reaction was 35%.

Synthesis of **S-** (P(TFEMA-*r*-SEMA)). SEMA (4.00g, 20.6 mmol), and TFEMA (4.00g, 23.8 mmol) were dissolved in this order in DMSO (32 mL). AIBN (0.008g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 60° C, while stirring at 300 rpm for 17 hours. The flask was removed from the oil bath and unsealed, and 0.8 g of MEHQ was added to terminate the reaction. The reaction mixture was then precipitated in 1:3 ethanol to hexane volume ratio and purified by stirring two fresh portions of 2:3 ethanol to hexane volume ratio for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72h at 60 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 25), using the ratio of protons from the two different monomer units. The calculated composition was: 37 mol% SEMA, and 63 mol% TFEMA. The final conversion of this reaction was 55%.

After both syntheses, thin film composite membranes were prepared using both copolymers A2+ and S-. Each copolymer (0.5 g) was dissolved separately in methanol (9.5 g) at approximately 25° C. Both copolymer solutions were passed through 0.45 micrometer syringe filters (Whatman) and degassed in a vacuum oven for at least 1 hour. The membranes were prepared by coating a thin layer of each copolymer solution at a time on top of a commercial ultrafiltration (UF) membrane using a film applicator rod, additionally, in between coatings a 10 min solvent evaporation period was adopted. When S- was coated first the membrane was named **SA2**, and when A2+ was coated first the membrane was named **A2S**. PS35 (**PSf**) ultrafiltration membrane, purchased from Solecta (Oceanside, Calif.), was used as the base membrane. After coating, the membrane was immersed in a water bath.

Film thickness and morphology was determined by the examination of freeze-fractured cross-sections of the membranes using a scanning electron microscope. The coating layer can be observed with a thickness of about 0.5 micrometers. FIG. 26.

Example 14
Water permeance of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A2+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the pure water fluxes through the membranes described in example 13 were measured using an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. After a stabilization period of at least one hour, a sample of the permeate was collected over 120 minutes and weighed. The value obtained was divided by filtration area and experiment time to obtain flux. The flux value was normalized by pressure to obtain pure water permeance. The permeance of A2S was 8.5 ± 0.9 L/m^2.h.bar. While the permeance of A2+ (only A2+ is coated) was 59 ± 11 L/m^2.h.bar. These membranes have permeances comparable to nanofiltration and ultrafiltration commercial membranes.

Example 15
Neutral solute rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A2+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membranes prepared as described in example 13 were used in experiments aimed at identifying their effective pore size, or size cut-off. Dye molecules and sugars were used to probe this property. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a 0.1 mM solution of the probe dye (vitamin B12 (B12), or riboflavin (Rib)); or 4000 ppm solution of sugar molecule (sucrose, or glucose) or glycerol in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by COD kits (K-7365, CHEMetrics), or UV–vis spectrometer (Genesys10, ThermoScientific) and the solute rejection (%) was calculated (FIG.s 27-28). The cell was rinsed several times with water. Pure water was filtered through the membrane until the permeate was completely clear before switching to a new solute.

Example 16

Salt rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A2+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membranes prepared as described in example 13 were used in experiments to determine their salt retention properties. Different salts at different concentrations were used to probe this property, their concentrations were easily measured by a standard conductivity probe. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a solution of the probe salt in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by the conductivity probe and the salt rejection (%) was calculated (FIG.s 29-31). The cell was rinsed several times with water. Pure water was filtered through the membrane until the permeate volume reaches 1 mL before switching to a new salt solution.

Example 17

Synthesis and membrane preparation of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S2-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) is synthesized using a higher content of TFEMA (**S2-**). While the cationic copolymer is the same A+ copolymer described in example 1.

Synthesis of **A+** (P(TFEMA-*r*-MAETA)). MAETA (4.00g, 19.3 mmol), and TFEMA (4.00g, 23.8 mmol) were dissolved in this order in DMSO (32 mL). AIBN (0.008g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 60° C, while stirring at 300 rpm for 17 hours. The flask was removed from the oil bath and unsealed, and 0.8 g of MEHQ was added to terminate the reaction. The reaction mixture was then precipitated in acetone and purified by stirring two fresh portions of 1:3 ethanol to hexane volume ratio for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72h at 60 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 32), using the ratio of protons from the two different monomer units. The calculated

composition was: 41 mol% MAETA, and 59 mol% TFEMA. The final conversion of this reaction was 45%.

Synthesis of **S2-** (P(TFEMA-*r*-SEMA)). SEMA (1.75g), and TFEMA (3.25g) were dissolved in this order in DMSO (20 mL). AIBN (0.005g) was added to the flask. The flask was sealed, and nitrogen was bubbled through the reaction mixture for 30 minutes to purge any dissolved oxygen. The flask was then placed in an oil bath set to 60° C, while stirring at 300 rpm for 17 hours. The flask was removed from the oil bath and unsealed, and 0.5 g of MEHQ was added to terminate the reaction. The reaction mixture was then precipitated in DI water and purified by stirring two fresh portions of DI water for at least 3 hours. The copolymer was dried in the vacuum oven for 48h at 60 °C. After that the copolymer was purified by stirring two fresh portions of hexane for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72h at 60 °C. The composition of the copolymer was calculated from the ^{1}H-NMR spectrum (FIG. 33), using the ratio of protons from the two different monomer units. The calculated composition was: 30 mol% SEMA, and 70 mol% TFEMA. The final conversion of this reaction was 21%.

After both syntheses, thin film composite membranes were prepared using both copolymers A+ and S2-. Each copolymer (0.5 g) was dissolved separately in methanol (9.5 g) at approximately 25° C. Both copolymer solutions were degassed in a vacuum oven for at least 1 hour. The membranes were prepared by coating a thin layer of each copolymer solution at a time on top of a commercial ultrafiltration (UF) membrane using a film applicator rod, additionally, in between coatings a 10 min solvent evaporation period was adopted. When S2- was coated first the membrane was named **S2A**, and when A+ was coated first the membrane was named **AS2**. PS35 (**PSf**) ultrafiltration membrane, purchased from Solecta (Oceanside, Calif.), was used as the base membrane. After coating, the membrane was immersed in a water bath.

Film thickness and morphology was determined by the examination of freeze-fractured cross-sections of the membranes using a scanning electron microscope. The coating layer can be observed with a thickness of about 0.4 micrometers. FIG. 34.

Example 18
Water permeance of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S2-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the pure water fluxes through the membranes described in example 17 were measured using an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. After a stabilization period of at least one hour, a sample of the permeate was collected over 120 minutes and weighed. The value obtained was divided by filtration area and experiment time to obtain flux. The flux value was normalized by pressure to obtain pure water permeance. The permeance of AS2 was 4.7 ± 0.8 L/m^2.h.bar. While the permeance of S2- (only S2- is coated) was 98 ± 17 L/m^2.h.bar. These membranes have permeances comparable to nanofiltration and ultrafiltration commercial membranes.

Example 19
Neutral solute rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S2-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membranes prepared as described in example 17 were used in experiments aimed at identifying their effective pore size, or size cut-off. Dye molecules were used to probe this property. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a 0.1 mM water solution of the probe dye (vitamin B12 (B12), or riboflavin (Rib)) was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by UV–vis spectrometer (Genesys10, ThermoScientific) and the solute rejection (%) was calculated (FIG. 35). The cell was rinsed several times with water. Pure water was filtered through the membrane until the permeate was completely clear before switching to a new solute.

Example 20

Salt rejection of Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-(methacryloyloxy)ethyl]trimethylammonium chloride) (A+) and Poly (2,2,2-trifluoroethyl methacrylate)-random- poly (2-sulfoethyl methacrylate) (S2-) used as an Amphiphilic Polyelectrolyte Complex (APEC) multilayer

In this example, the membranes prepared as described in example 17 were used in experiments to determine their salt retention properties. Different salts at different concentrations were used to probe this property, their concentrations were easily measured by a standard conductivity probe. The retention experiments were performed on an Amicon 8010 stirred, dead-end filtration cell (Millipore) with a cell volume of 10 mL and an effective filtration area of 4.1 cm^2. The cell was stirred at 500 rpm, and the test was performed at 40 psi. The cell was stirred at 500 rpm to minimize concentration polarization effects. After running pure water through the membrane for at least an hour, the cell was emptied, and a solution of the probe salt in water was placed in the cell. After rejecting the first 1 mL, to avoid pure water contamination, enough volume was collected for analysis by the conductivity probe and the salt rejection (%) was calculated (FIG.s 36-38). The cell was rinsed several times with water. Pure water was filtered through the membrane until the permeate volume reaches 1 mL before switching to a new salt solution.

INCORPORATION BY REFERENCE

All publications and patents mentioned herein are hereby incorporated by reference in their entirety as if each individual publication or patent was specifically and individually indicated to be incorporated by reference. In case of conflict, the present application, including any definitions herein, will control.

EQUIVALENTS

While specific embodiments of the subject invention have been discussed, the above specification is illustrative and not restrictive. Many variations of the invention will become apparent to those skilled in the art upon review of this specification and the claims below. The full scope of the invention should be determined by reference to the claims, along with their full scope of equivalents, and the specification, along with such variations.

CLAIMS

We claim:

1. A composite membrane, comprising a porous support; and a selective layer comprising a first copolymer and a second copolymer; wherein:
the first copolymer comprises a first plurality of hydrophobic repeat units and a plurality of cationic repeat units;
the second copolymer comprises a second plurality of hydrophobic repeat units and a plurality of anionic repeat units; and
the first copolymer and the second copolymer are essentially insoluble in water (*e.g.,* under operating conditions).

2. The composite membrane of claim 1, wherein the first copolymer and the second copolymer are insoluble in water (*e.g.,* under operating conditions).

3. The composite membrane of claim 1, wherein the composite membrane is a thin film composite membrane.

4. The composite membrane of any one of claims 1-3, wherein the composite membrane has a thickness of about 20 μm to about 1,000 μm.

5. The composite membrane of any one of claims 1-3, wherein the composite membrane has a thickness of about 50 μm to about 200 μm.

6. The composite membrane of any one of claims 1-5, wherein the selective layer has a thickness of about 30 nm to about 5 μm.

7. The composite membrane of any one of claims 1-6, wherein the selective layer has a thickness of about 30 nm to about 1,000 nm.

8. The composite membrane of any one of claims 1-7, wherein the selective layer has a thickness of about 10 nm, about 25 nm, about 50 nm, about 75 nm, about 100 nm, about 125 nm, about 150 nm, about 175 nm, about 200 nm, about 225 nm, about 250 nm, about 275 nm, about 300 nm, about 325 nm, about 350 nm, about 375 nm, about 400 nm, about 425 nm,

about 450 nm, about 475 nm, about 500 nm, about 525 nm, about 550 nm, about 575 nm, or about 600 nm.

9. The composite membrane of any one of claims 1-8, wherein the selective layer has a thickness of about 400 nm, about 425 nm, about 450 nm, about 475 nm, about 500 nm, about 525 nm, about 550 nm, about 575 nm, or about 600 nm.

10. The composite membrane of any one of claims 1-9, wherein the plurality of cationic repeat units is partially positively charged in water (*e.g.,* in water at a neutral pH or in water under operating conditions).

11. The composite membrane of any one of claims 1-9, wherein the plurality of cationic repeat units is positively charged in water (*e.g.,* in water at a neutral pH or in water under operating conditions).

12. The composite membrane of any one of claims 1-11, wherein the plurality of anionic repeat units is partially negatively charged in water (*e.g.,* in water at a neutral pH or in water under operating conditions).

13. The composite membrane of any one of claims 1-11, wherein the plurality of anionic repeat units is negatively charged in water (*e.g.,* in water at a neutral pH or in water under operating conditions).

14. The composite membrane of any one of claims 1-13, wherein the selective layer consists essentially of the first copolymer and the second copolymer.

15. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 5 – 80 wt% of the plurality of cationic repeat units.

16. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 15 – 75 wt% of the plurality of cationic repeat units.

17. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 20 – 50 wt% of the plurality of cationic repeat units.

18. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 10 wt%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the plurality of cationic repeat units.

19. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 5 – 80 mol% of the plurality of cationic repeat units.

20. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 15 – 75 mol% of the plurality of cationic repeat units.

21. The composite membrane of any one of claims 1-14, wherein the first copolymer comprises about 20 – 50 mol% of the plurality of cationic repeat units.

22. The composite membrane of any one of claims 1-21, wherein the first copolymer comprises about 10 mol%, about 20 mol%, about 30 mol%, about 40 mol%, about 50 mol%, about 60 mol%, about 70 mol%, or about 80 mol% of the plurality of cationic repeat units.

23. The composite membrane of any one of claims 1-21, wherein the first copolymer comprises about 10 wtl%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the first plurality of hydrophobic repeat units.

24. The composite membrane of any one of claims 1-21, wherein the first copolymer comprises about 10 mol%, about 20 mol%, about 30 mol%, about 40 mol%, about 50 mol%, about 60 mol%, about 70 mol%, or about 80 mol% of the first plurality of hydrophobic repeat units.

25. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 5 – 80 wt% of the plurality of anionic repeat units.

26. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 15 – 75 wt% of the plurality of anionic repeat units.

27. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 20 – 50 wt% of the plurality of anionic repeat units.

28. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 10 wt%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the plurality of anionic repeat units.

29. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 5 – 80 mol% of the plurality of anionic repeat units.

30. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 15 – 75 mol% of the plurality of anionic repeat units.

31. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 20 – 50 mol% of the plurality of anionic repeat units.

32. The composite membrane of any one of claims 1-24, wherein the second copolymer comprises about 10 mol%, about 20 mol%, about 30 mol%, about 40 mol%, about 50 mol%, about 60 mol%, about 70 mol%, or about 80 mol% of the plurality of anionic repeat units.

33. The composite membrane of any one of claims 1-32, wherein the second copolymer comprises about 10 wt%, about 20 wtl%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, or about 80 wt% of the first plurality of hydrophobic repeat units.

34. The composite membrane of any one of claims 1-32, wherein the second copolymer comprises about 10 mol%, about 20 mol%, about 30 mol%, about 40 mol%, about 50 mol%, about 60 mol%, about 70 mol%, or about 80 mol% of second plurality of hydrophobic repeat units.

35. The composite membrane of any one of claims 1-34, wherein the first copolymer has an average molar mass of at least 30,000 g/mol.

36. The composite membrane of any one of claims 1-37, wherein the first copolymer has an average molar mass of at least 50,000 g/mol.

37. The composite membrane of any one of claims 1-34, wherein the first copolymer has an average molar mass of at least 100,000 g/mol.

38. The composite membrane of any one of claims 1-34, wherein the first copolymer has an average molar mass of 20,000 g/mol to about 500,000 g/mol.

39. The composite membrane of any one of claims 1-34, wherein the first copolymer has an average molar mass of 30,000 g/mol to about 500,000 g/mol.

40. The composite membrane of any one of claims 1-34, wherein the first copolymer has an average molar mass of 50,000 g/mol to about 500,000 g/mol.

41. The composite membrane of any one of claims 1-34, wherein the first copolymer has an average molar mass of 100,000 g/mol to about 500,000 g/mol.

42. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of at least 30,000 g/mol.

43. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of at least 50,000 g/mol.

44. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of at least 100,000 g/mol.

45. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of 20,000 g/mol to about 500,000 g/mol.

46. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of 30,000 g/mol to about 500,000 g/mol.

47. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of 50,000 g/mol to about 500,000 g/mol.

48. The composite membrane of any one of claims 1-41, wherein the second copolymer has an average molar mass of 100,000 g/mol to about 500,000 g/mol.

49. The composite membrane of any one of claims 1-48, wherein the first copolymer and the second copolymer are sequentially layered on the porous support (*e.g.,* the first copolymer and the second copolymer have been applied to the porous support layer sequentially).

50. The composite membrane of claim 49, wherein the first copolymer is the first layer (*e.g.,* the outermost layer) and the second copolymer is the second layer (*e.g.,* the first copolymer layer is on the second copolymer layer and the second copolymer layer is in contact with the porous support).

51. The composite membrane of claim 49, wherein the second copolymer is the first layer (*e.g.,* the outermost layer) and the first copolymer is the second layer (*e.g.,* the second copolymer layer is on the first copolymer layer and the first copolymer layer is in contact with the porous support).

52. The composite membrane of any one of claims 1-48, wherein the first copolymer and the second copolymer are intermingled on the porous support (*e.g.,* the first copolymer and the second copolymer form a homogenous layer on the porous support).

53. The composite membrane of any one of claims 1-52, wherein the first plurality of hydrophobic repeat units comprises repeat units derived from acrylates (*e.g.,* alkyl acrylates, fluorinated acrylates or methacrylates), acrylamides (*e.g.,* fluorinated acrylamides), styrene, or hydrophobic amino acids.

54. The composite membrane of any one of claims 1-52, wherein the first plurality of hydrophobic repeat units comprises repeat units derived from methacrylate.

55. The composite membrane of any one of claims 1-52, wherein the first plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA), pentafluoropropyl methacrylate, heptafluorobutyl, pentafluorophenyl methacrylate, styrene, methyl methacrylate, acrylonitrile, 2-chloroethyl methacrylate, 2-bromoethyl methacrylate, and allyl methacrylate.

56. The composite membrane of any one of claims 1-52, wherein the first plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA).

57. The composite membrane of any one of claims 1-56, wherein the second plurality of hydrophobic repeat units comprises repeat units derived from acrylates (*e.g.,* alkyl acrylates, fluorinated acrylates or methacrylates), acrylamides (*e.g.,* fluorinated acrylamides), styrene, or hydrophobic amino acids.

58. The composite membrane of any one of claims 1-56, wherein the second plurality of hydrophobic repeat units comprises repeat units derived from methacrylate.

59. The composite membrane of any one of claims 1-56, wherein the second plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA), pentafluoropropyl methacrylate, heptafluorobutyl, pentafluorophenyl methacrylate, styrene, methyl methacrylate, acrylonitrile, 2-chloroethyl methacrylate, 2-bromoethyl methacrylate, and allyl methacrylate.

60. The composite membrane of any one of claims 1-56, wherein the second plurality of hydrophobic repeat units comprises repeat units derived from 2,2-trifluoroethyl methacrylate (TFEMA).

61. The composite membrane of any one of claims 1-60, wherein the plurality of cationic repeat units comprises repeat units derived from acrylate, acrylamide, styrene, or vinyl monomers substituted with amine, pyridinium, imidazolium, phosphonium, or pyrrolidinium.

62. The composite membrane of any one of claims 1-60, wherein the plurality of cationic repeat units comprises repeat units derived from methacrylate.

63. The composite membrane of any one of claims 1-60, wherein the plurality of cationic repeat units comprises repeat units derived from [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MAETA), [3 (methacryloylamino)propyl] trimethylammonium chloride, [2-(acryloyloxy)ethyl] trimethylammonium chloride, (3-acrylamidopropyl)trimethylammonium chloride; 4-vinylbenzyl(triphenyl)phosphonium

chloride, (vinylbenzyl)trimethylammonium chloridemethacrylate, 3-vinylaniline, 4-vinylaniline, 2-isopropenylaniline, N-(3- aminopropyl)methacrylamide hydrochloride, N-vinylimidazolium, 1-allyl-3-vinylimidazoliums, 1-allyl-2methyl-5-vinyl-pyridinium, 1-allyl-5-vinyl-pyridinium, or 1-Methyl-1-(1-vinylcyclohexyl)pyrrolidinium iodide.

64. The composite membrane of any one of claims 1-60, wherein the plurality of cationic repeat units comprises repeat units derived from 2-(methacryloyloxy)ethyl]trimethylammonium chloride.

65. The composite membrane of any one of claims 1-64, wherein the plurality of anionic repeat units comprises repeat units derived from acrylate, acrylamide, styrene, or vinyl monomers substituted with carboxylic acid, sulfonate, or phosphate.

66. The composite membrane of any one of claims 1-64, wherein the plurality of anionic repeat units comprises repeat units derived from methacrylate.

67. The composite membrane of any one of claims 1-64, wherein the plurality of anionic repeat units comprises repeat units derived from methacrylic acid (MAA), 2-sulfoethyl methacrylate (SEMA), L-tryptophan-methacrylamide, D-tryptophan-methacrylamide, L or D-tryptophan-acrylamide, L or D-alanine-methacrylamide, L or D-alanine-acrylamide, L or D-valine-methacrylamide, L or D-valine-acrylamide, L or D-isoleucine-methacrylamide, L or D-isoleucine-acrylamide, L or D-allo-isoleucine-methacrylamide, L or D-allo-isoleucine-acrylamide, L or D-methionine-methacrylamide, L or D-methionine-acrylamide, L or D-phenylalanine-methacrylamide, L or D-phenylalanine-acrylamide, L or D-tyrosine-methacrylamide, L or D-tyrosine-acrylamide, L or D-histadine-methacrylamide, L or D-histadine-acrylamide, L or D-glutamic acid-methacrylamide, L or D-glutamic acid-methacrylamide, L or D-aspartic acid-acrylamide, L or D-aspartic acid-methacrylamide, acrylic acid, 2-carboxyethyl acrylate, mono-2-(methacryloyloxy)ethyl succinate, mono-2-(methacryloyloxy)ethyl maleate, sodium 4-vinylbenzenesulfonate, 2-acrylamido-2-methylpropane sulfonic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt, 2-acrylamido-2-methyl-1-propanesulfonic acid, 3-sulfopropyl acrylate potassium salt, 3-sulfopropyl methacrylate potassium salt, 3-vinylbenzoic acid, 4-vinylbenzoic acid, 2-vinylbenzoic acid, 4-(2- propenyl)benzoic acid, 2-methyl-2-propene-1-sulfonic acid sodium

salt, vinylsulfonic acid sodium salt, vinylphosphonic acid, or (4-ethenylphenyl)methylphosphonic acid.

68. The composite membrane of any one of claims 1-64, wherein the plurality of anionic repeat units comprises repeat units derived from 2-sulfoethyl methacrylate.

69. The composite membrane of any one of claims 1-64, wherein the plurality of anionic repeat units comprises repeat units derived from methacrylic acid.

70. The composite membrane of any one of claims 1-69, wherein the first copolymer is a statistical (*e.g.,* approximately random) copolymer.

71. The composite membrane of any one of claims 1-69, wherein the first copolymer is a random copolymer.

72. The composite membrane of any one of claims 1-69, wherein the first copolymer is a block copolymer.

73. The composite membrane of any one of claims 1-69, wherein the first copolymer is a graft copolymer or a comb-shaped copolymer.

74. The composite membrane of any one of claims 1-69, wherein the second copolymer is a statistical (*e.g.,* approximately random) copolymer.

75. The composite membrane of any one of claims 1-74, wherein the second copolymer is a random copolymer.

76. The composite membrane of any one of claims 1-74, wherein the second copolymer is a block copolymer.

77. The composite membrane of any one of claims 1-74, wherein the second copolymer is a graft copolymer or a comb-shaped copolymer.

78. The composite membrane of any one of claims 1-77, wherein the effective pore size of the composite membrane is less than the effective pore size of a membrane prepared by coating only the first copolymer or only the second copolymer on the same porous support.

79. The composite membrane of claim 78, wherein the effective pore size is quantified by measuring the rejection of a neutral (*e.g.,* uncharged) solute.

80. The composite membrane of any one of claims 1-79, wherein the first copolymer is crosslinked.

81. The composite membrane of any one of claims 1-80, wherein the second copolymer is crosslinked.

82. The composite membrane of any one of claims 1-81, wherein the first copolymer and the second copolymer are essentially insoluble in water under operating conditions.

83. The composite membrane of any one of claims 1-81, wherein the first copolymer and the second copolymer are essentially insoluble in water under operating conditions.

84. A method of separating a solute from a solution, comprising contacting the solution with a composite membrane of any one of claims 1-83.

85. The method of claim 84, wherein the solution is passed (*e.g.,* filtered) through the composite membrane.

86. The method of claim 84 or 85, wherein the solute is a salt (*e.g.,* sodium chloride).

87. A method of fabricating the composite membrane of any one of claims 1-83, comprising applying a first copolymer as defined in any one of claims 8-11, 15-24, and 35-41; and applying a second copolymer as defined in any one of claims 11, 12, 25-34, and 42-48 to a porous support, thereby fabricating the composite membrane of any one of claims 1-83.

88. The method of claim 87, wherein the first copolymer and the second copolymer are applied to the porous support layer sequentially, thereby forming a bilayer membrane.

89. The method of claim 88, wherein the first copolymer is applied first, and the second copolymer is applied second.

90. The method of claim 88, wherein the first copolymer is applied second, and the second copolymer is applied first.

91. The method of claim 87, wherein the first copolymer and the second copolymer are applied to the porous support layer as a blend (*e.g.,* the first copolymer and second copolymer are mixed before application), thereby forming a blend membrane.

92. The method of any one of claims 87-91, wherein the first copolymer is dissolved in a protic solvent (*e.g.,* methanol) prior to application.

93. The method of any one of claims 87-92, wherein the second copolymer is dissolved in a protic solvent (*e.g.,* methanol) prior to application.

94. The method of any one of claims 87-93, wherein the first copolymer and the second copolymer are each dissolved in a protic solvent (*e.g.,* methanol) prior to application.

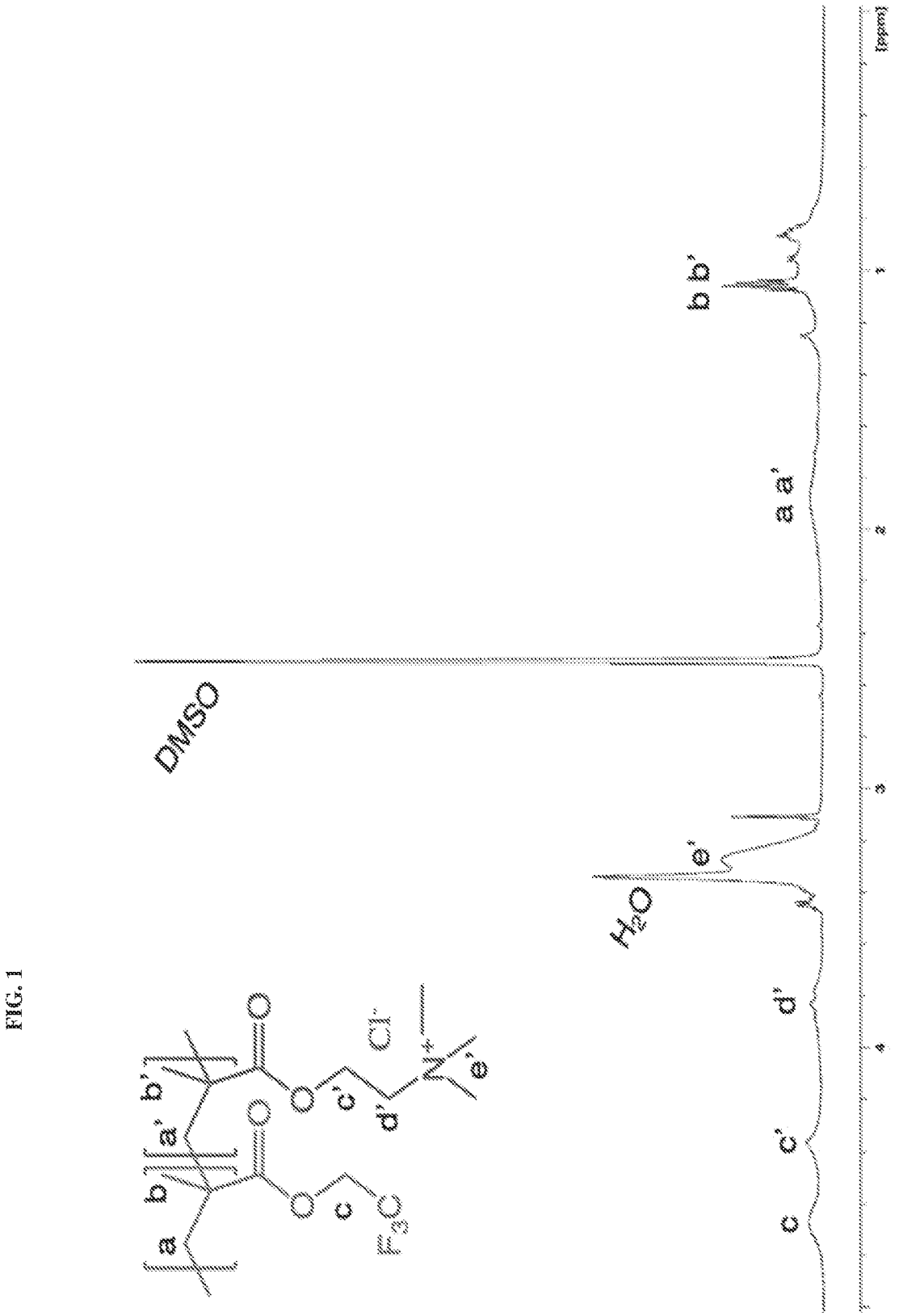

DMSO
H2O
a a'
b b'
c c'
d'
e'
a
b
a'
b'
c
c'
d'
e'
Cl-
N+
F3C
O
O
O

FIG. 2

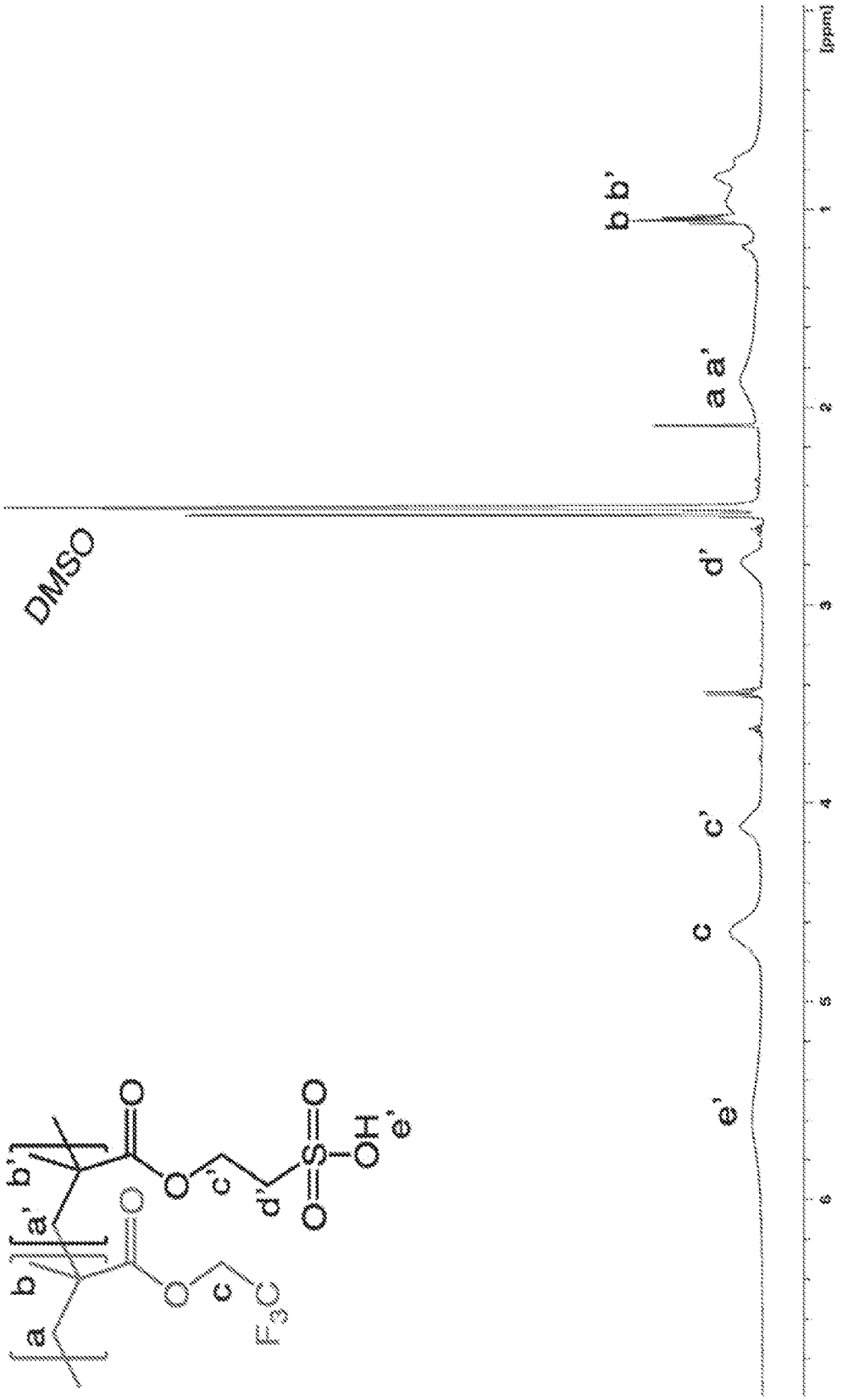


FIG. 3

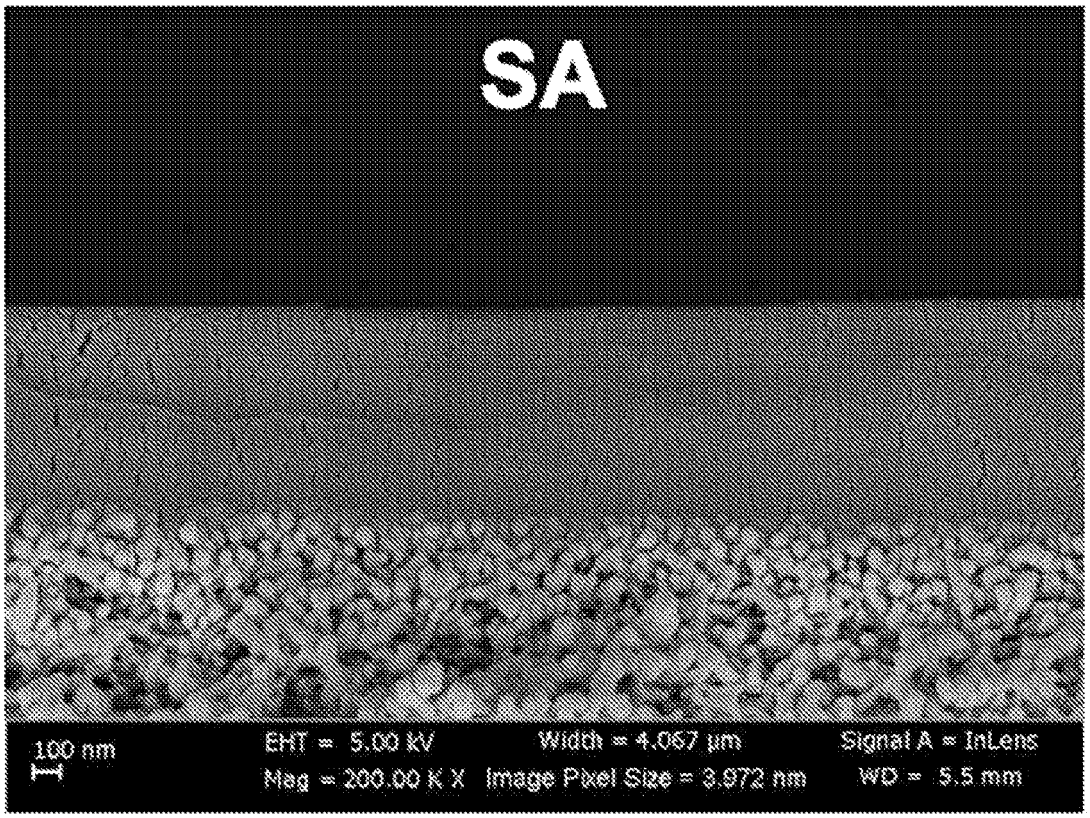

SA
100 nm
EHT = 5.00 kV
Width = 4.067 µm
Signal A = InLens
Mag = 200.00 K X
Image Pixel Size = 3.972 nm
WD = 5.5 mm

FIG. 4

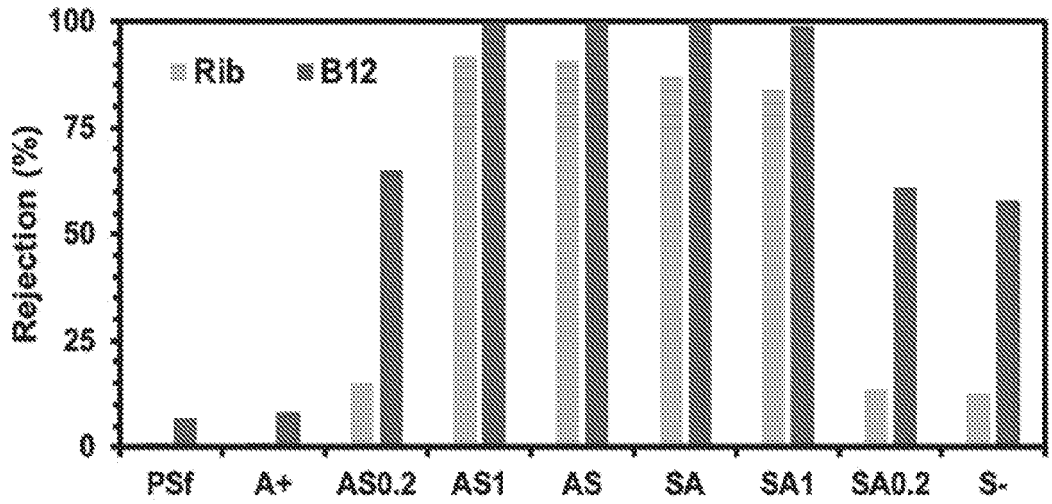

Rejection (%)
100
75
50
25
0
Rib
B12
PSf
A+
AS0.2
AS1
AS
SA
SA1
SA0.2
S-

FIG. 5

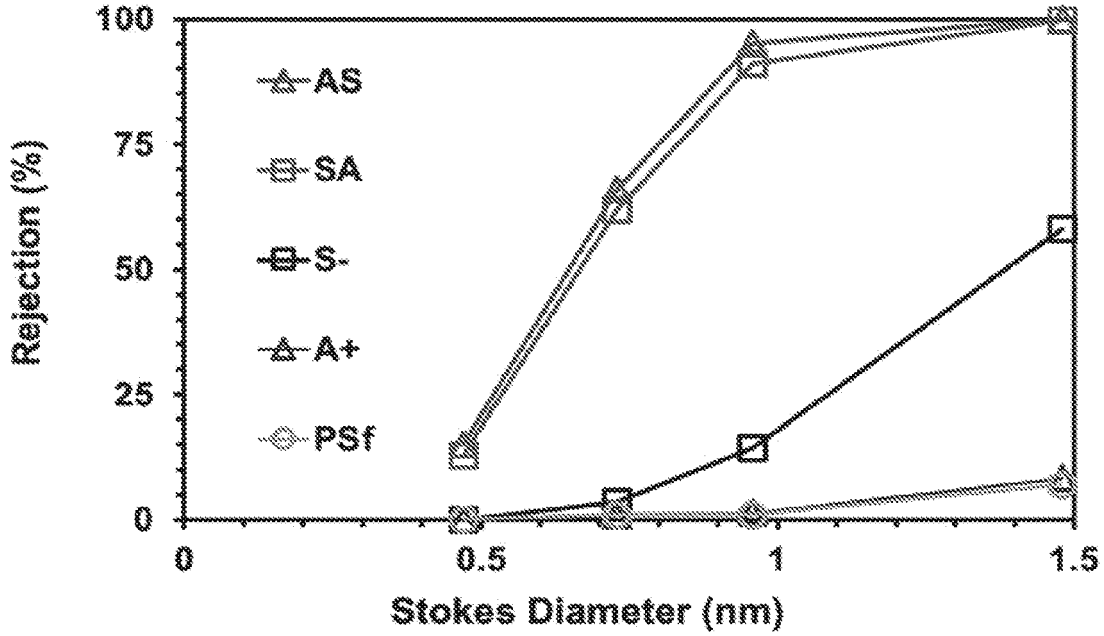

100
75
50
25
0
Rejection (%)
AS
SA
S-
A+
PSf
0
0.5
1
1.5
Stokes Diameter (nm)

FIG. 6

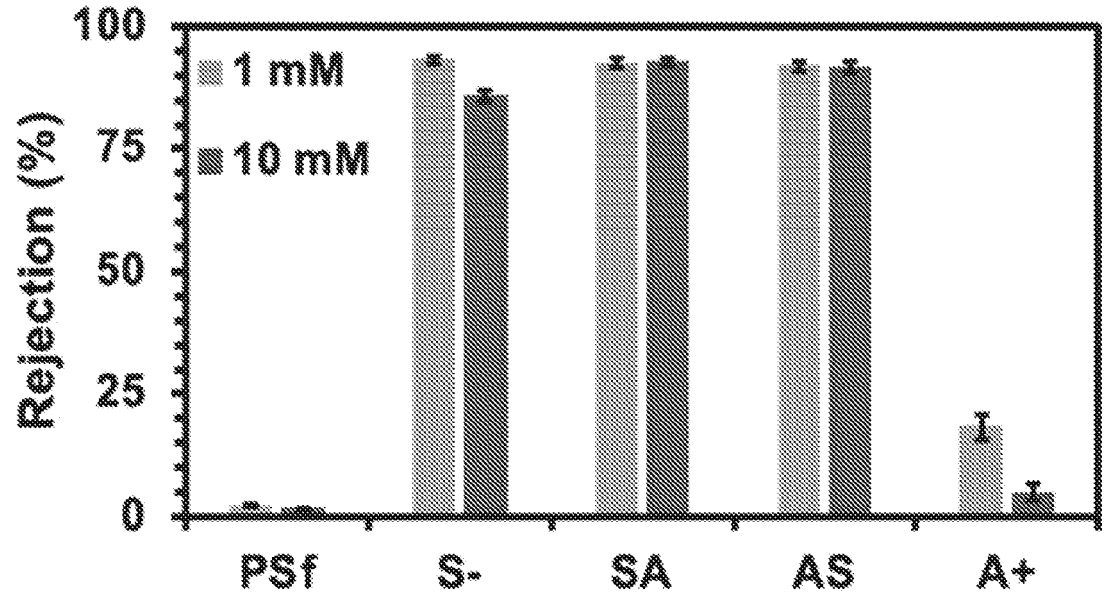

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
SA
AS
A+

FIG. 7

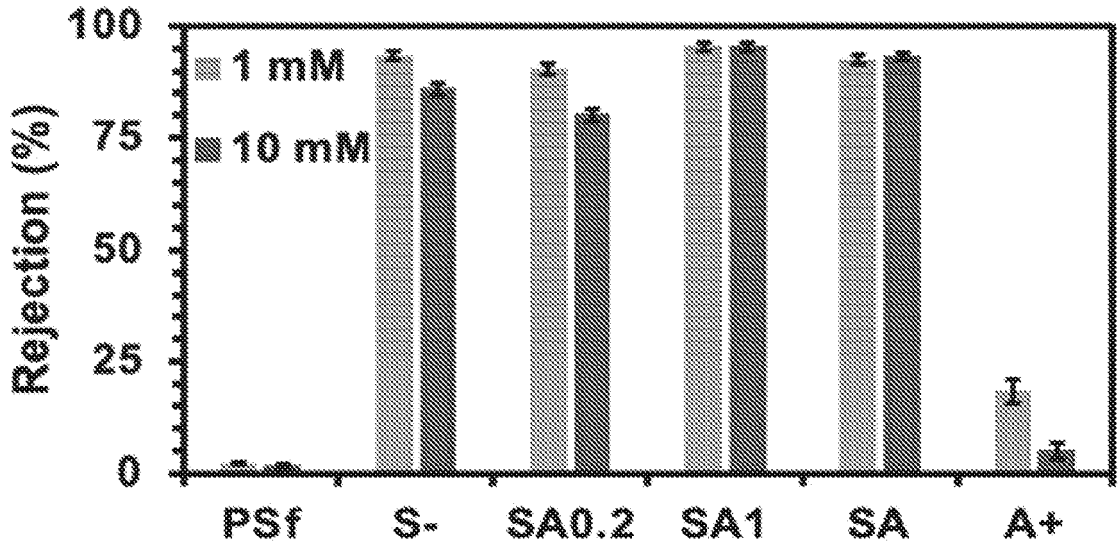

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
SA0.2
SA1
SA
A+

FIG. 8

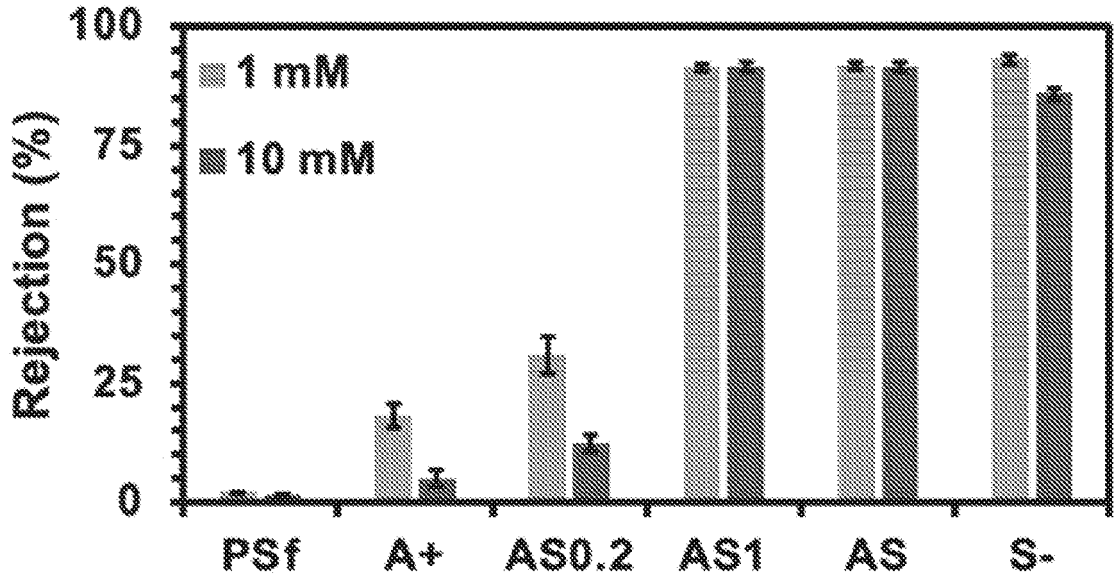

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
A+
AS0.2
AS1
AS
S-

FIG. 9

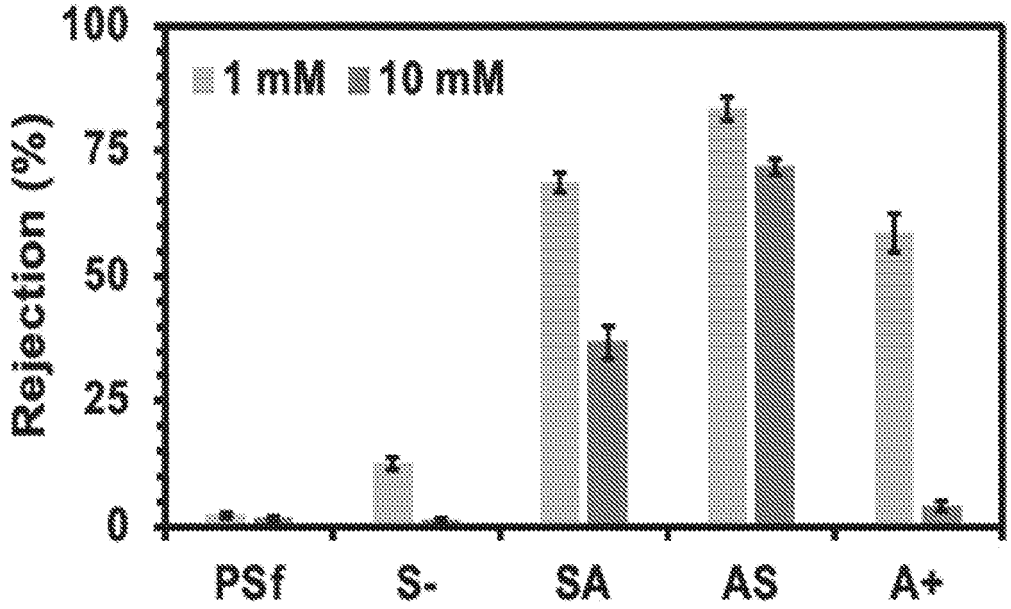


FIG. 10

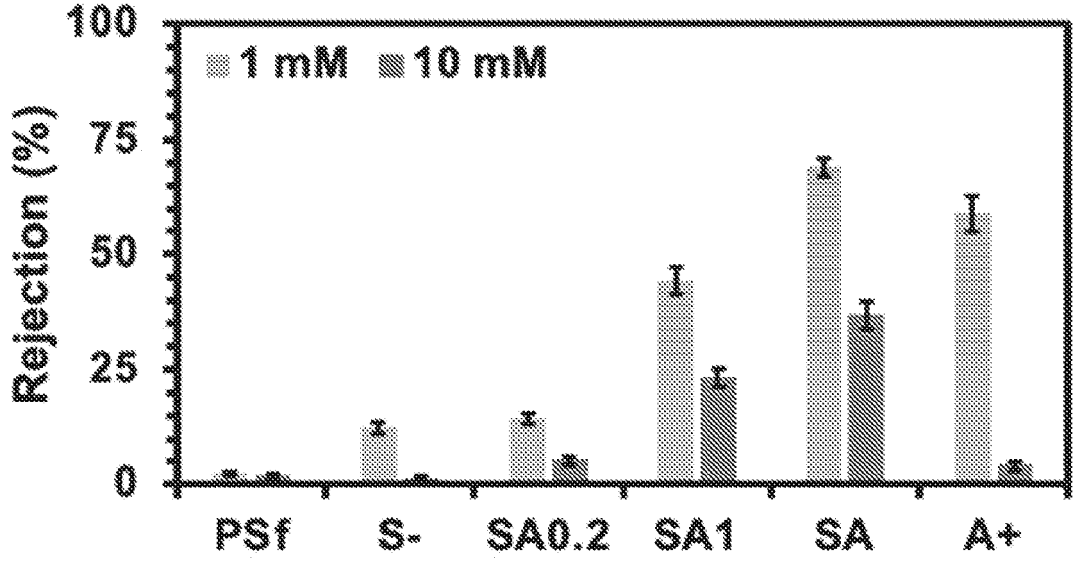

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
SA0.2
SA1
SA
A+

FIG. 11

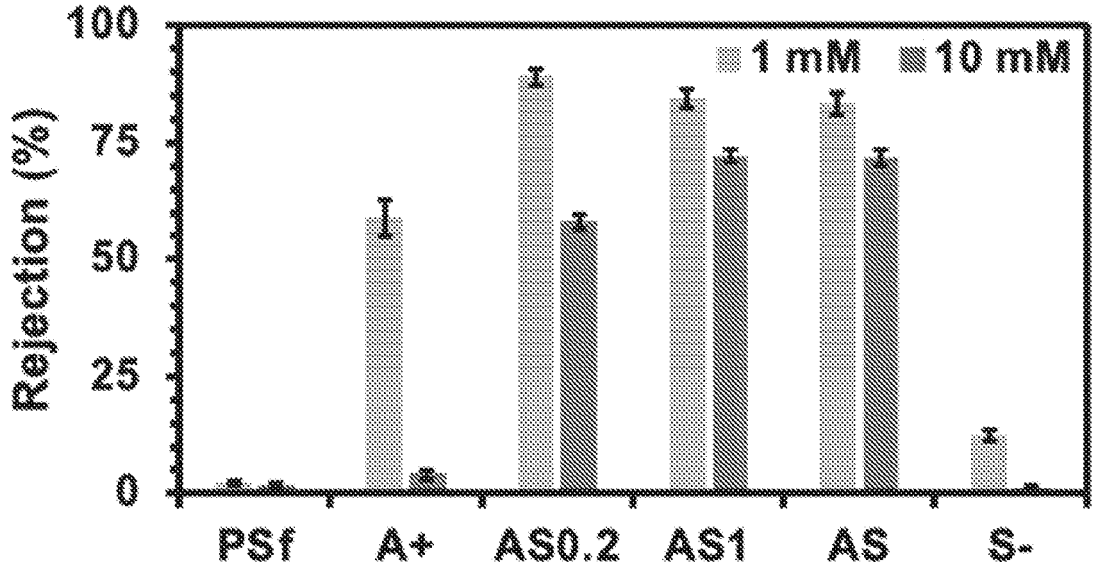

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
A+
AS0.2
AS1
AS
S-

FIG. 12

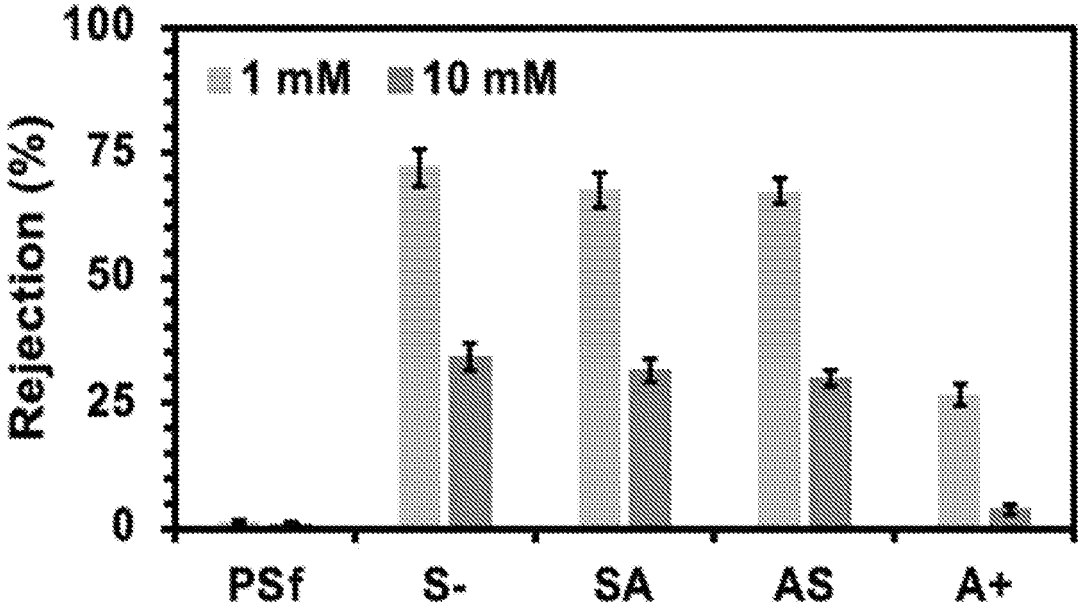


FIG. 13

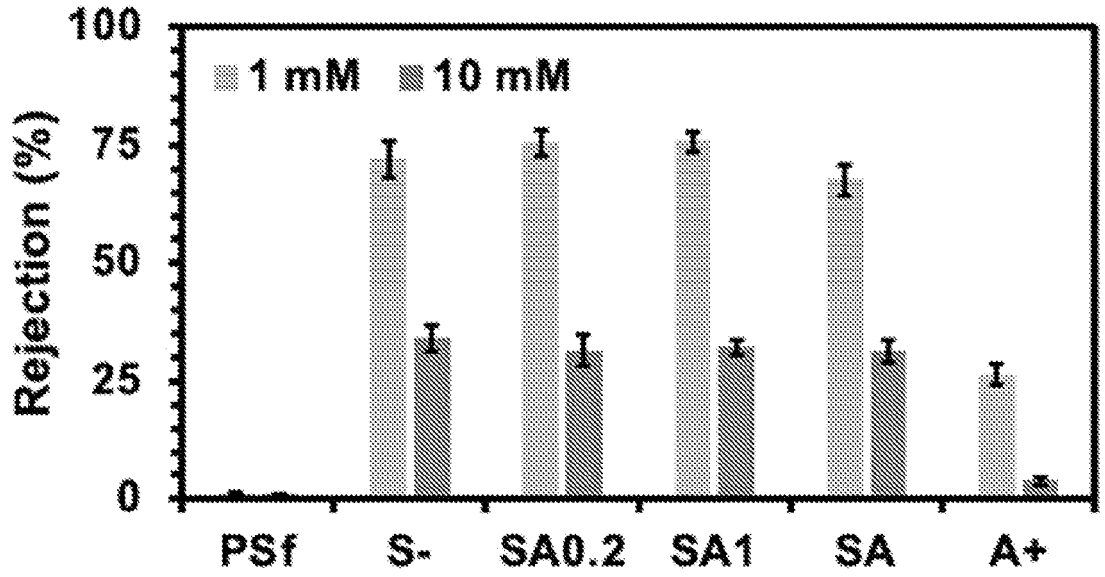

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
SA0.2
SA1
SA
A+

FIG. 14

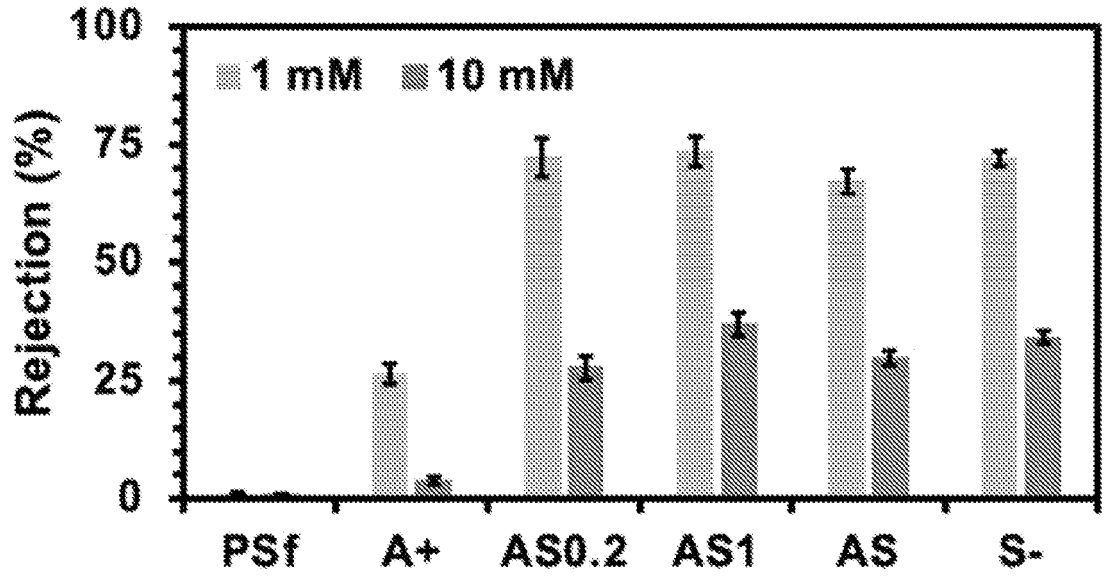
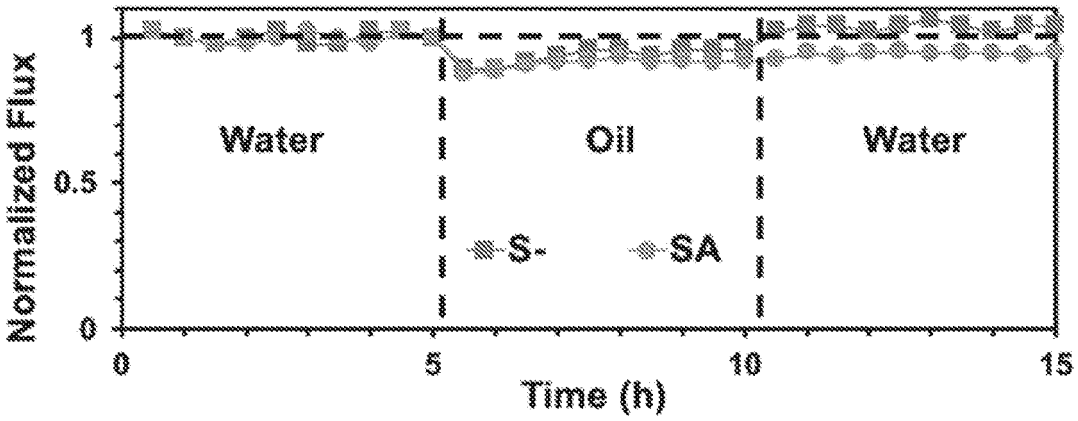

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
A+
AS0.2
AS1
AS
S-

FIG. 15



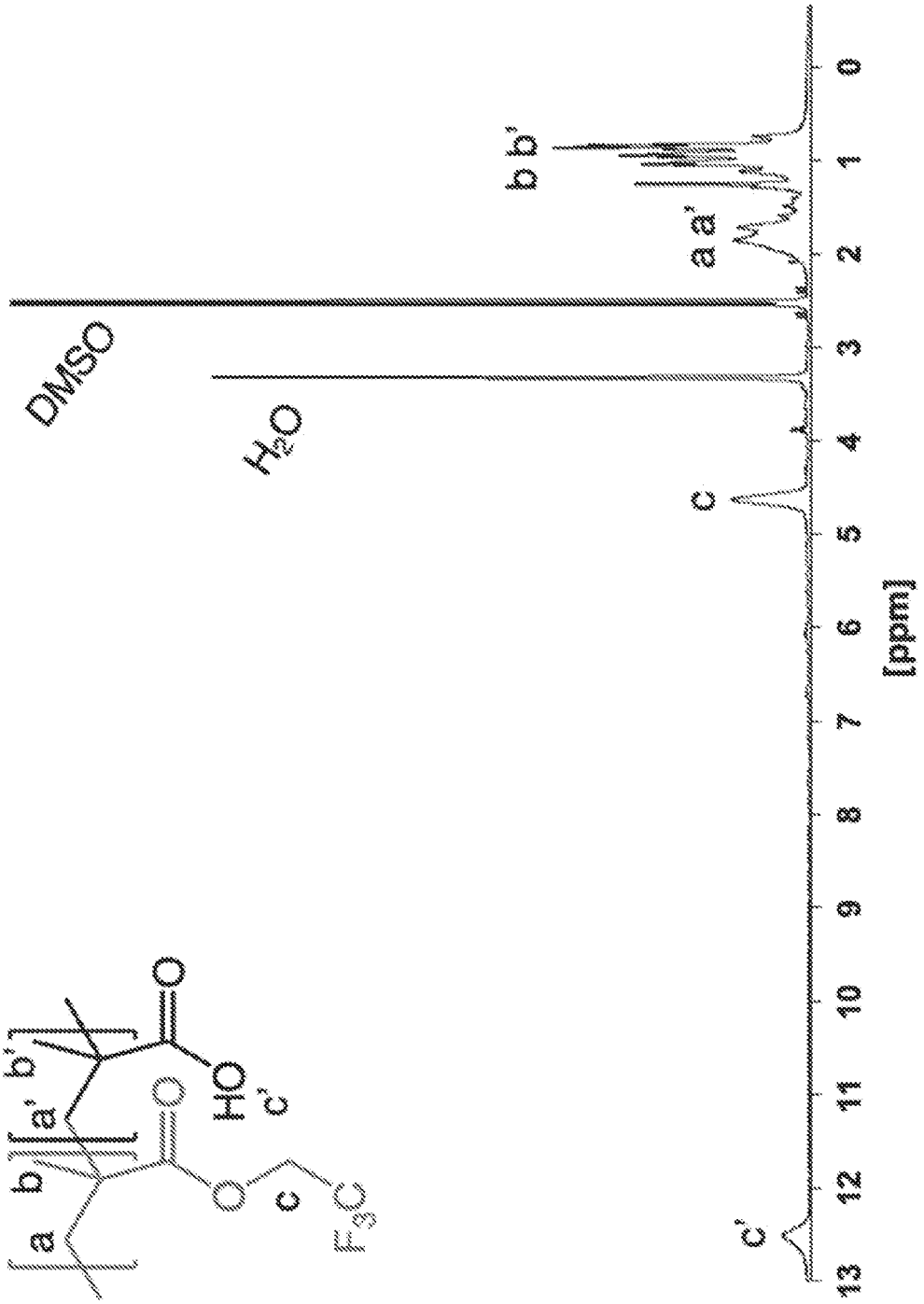


FIG. 16

FIG. 17

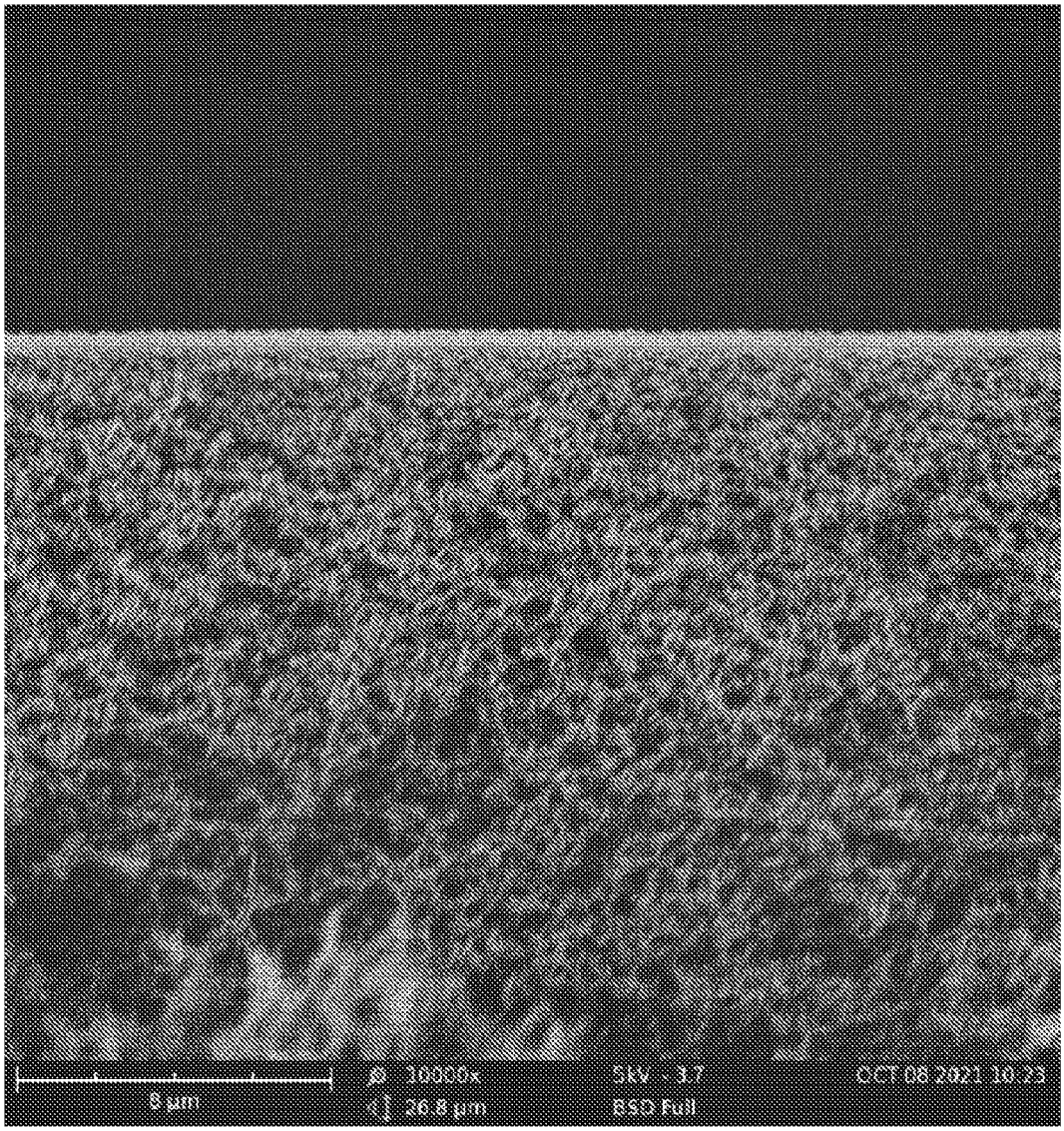


FIG. 18

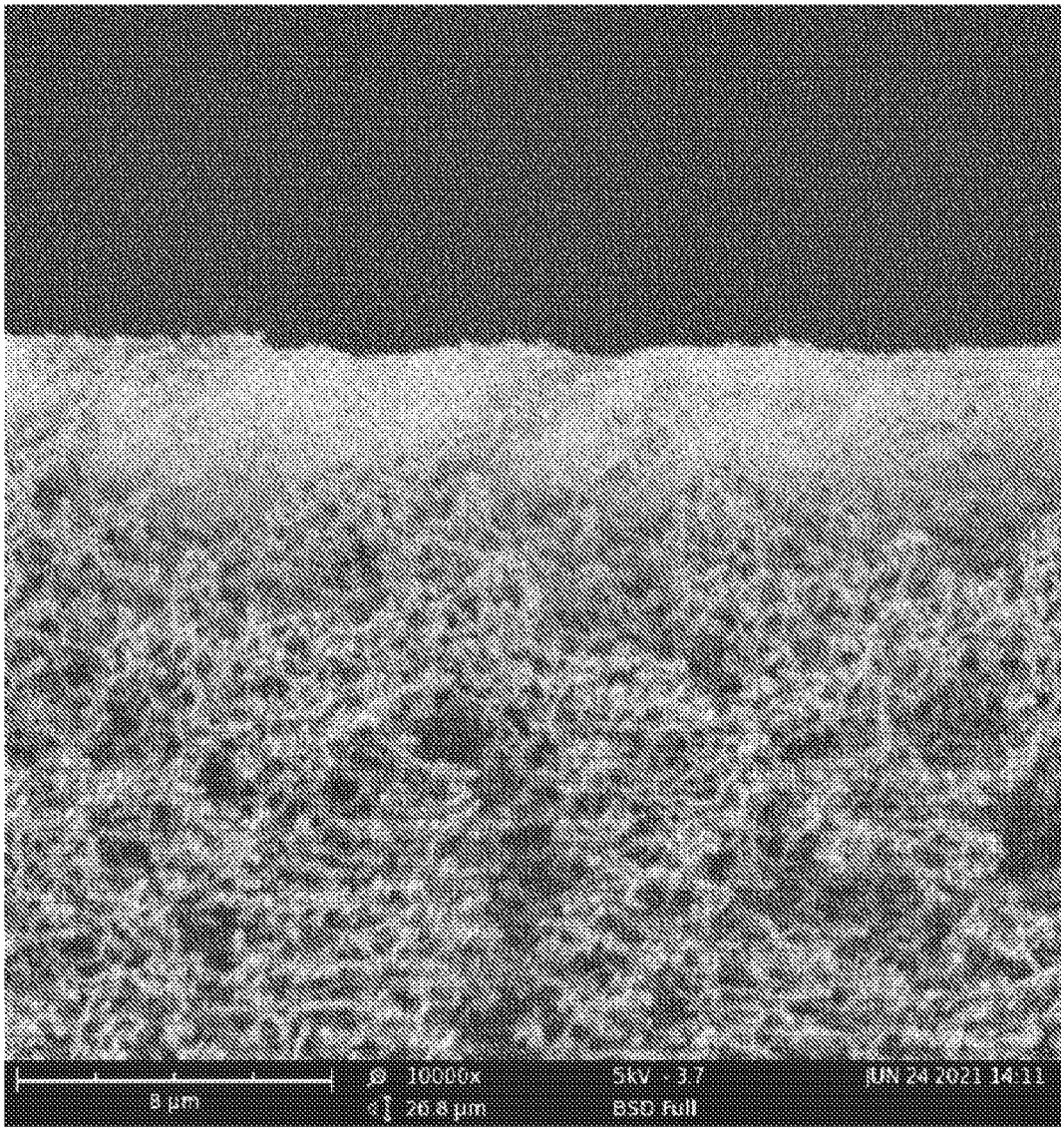


FIG. 19

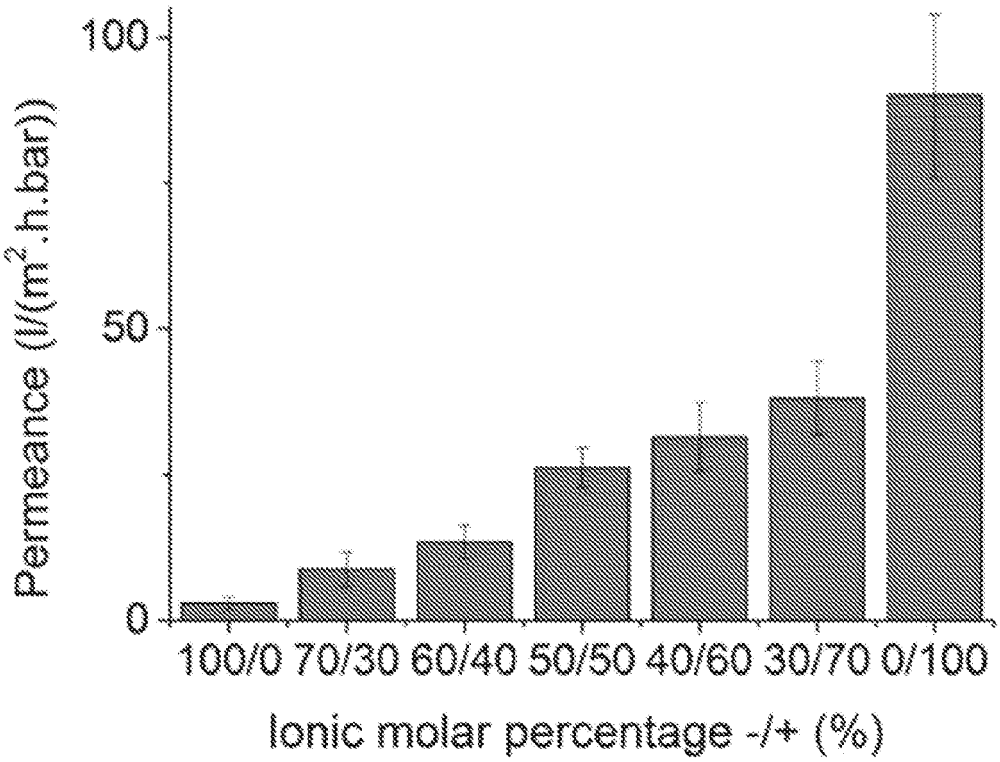

100
50
0
Permeance (l/(m2.h.bar))
100/0 70/30 60/40 50/50 40/60 30/70 0/100
Ionic molar percentage -/+ (%)

FIG. 20

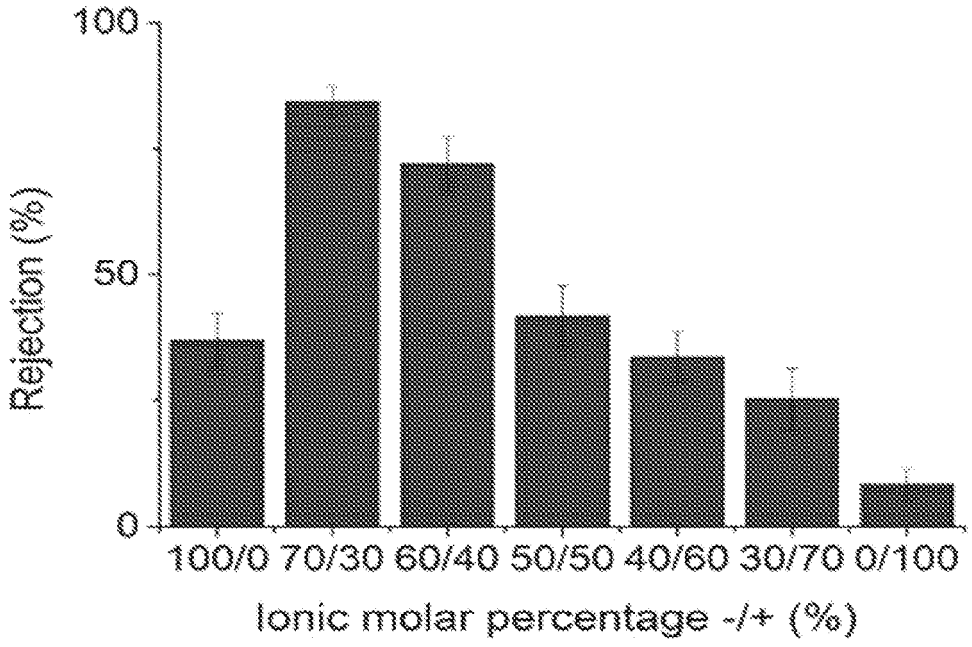

100
50
0
Rejection (%)
100/0 70/30 60/40 50/50 40/60 30/70 0/100
Ionic molar percentage -/+ (%)

FIG. 21

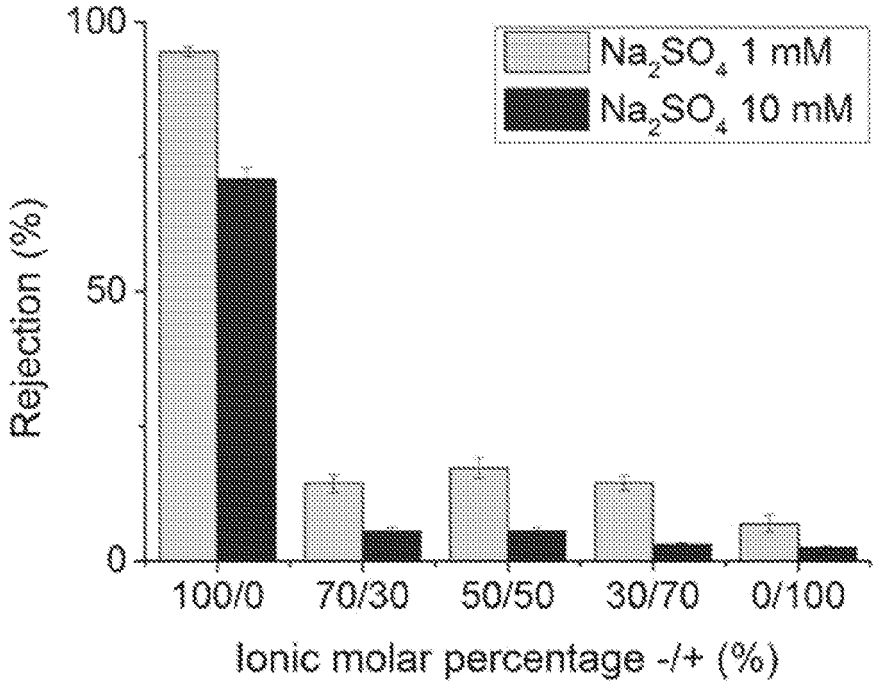

100
50
0
Rejection (%)
Na_2SO_4 1 mM
Na_2SO_4 10 mM
100/0
70/30
50/50
30/70
0/100
Ionic molar percentage -/+ (%)

FIG. 22

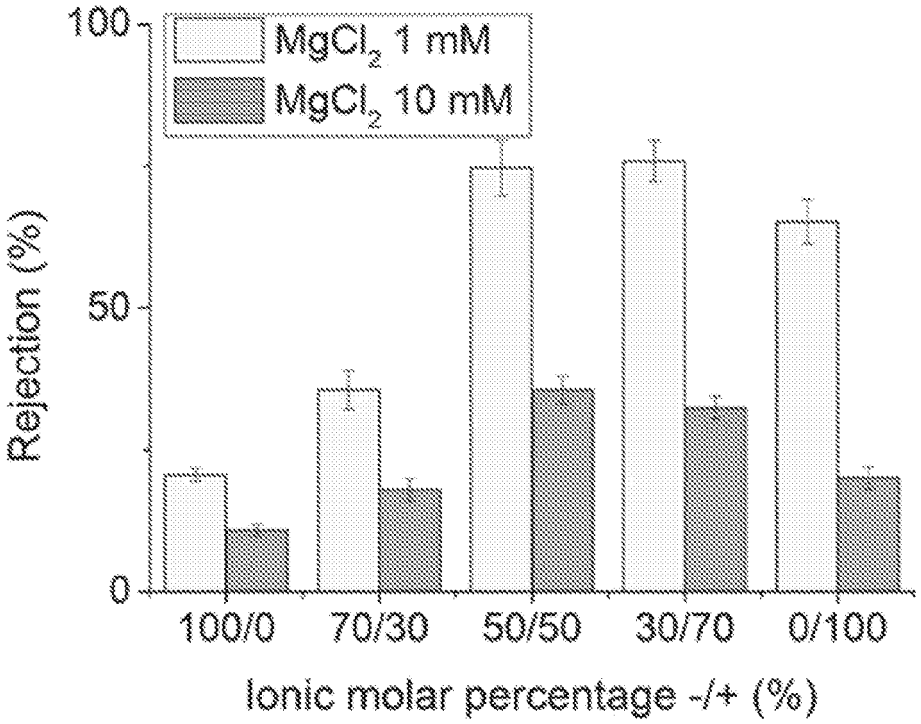
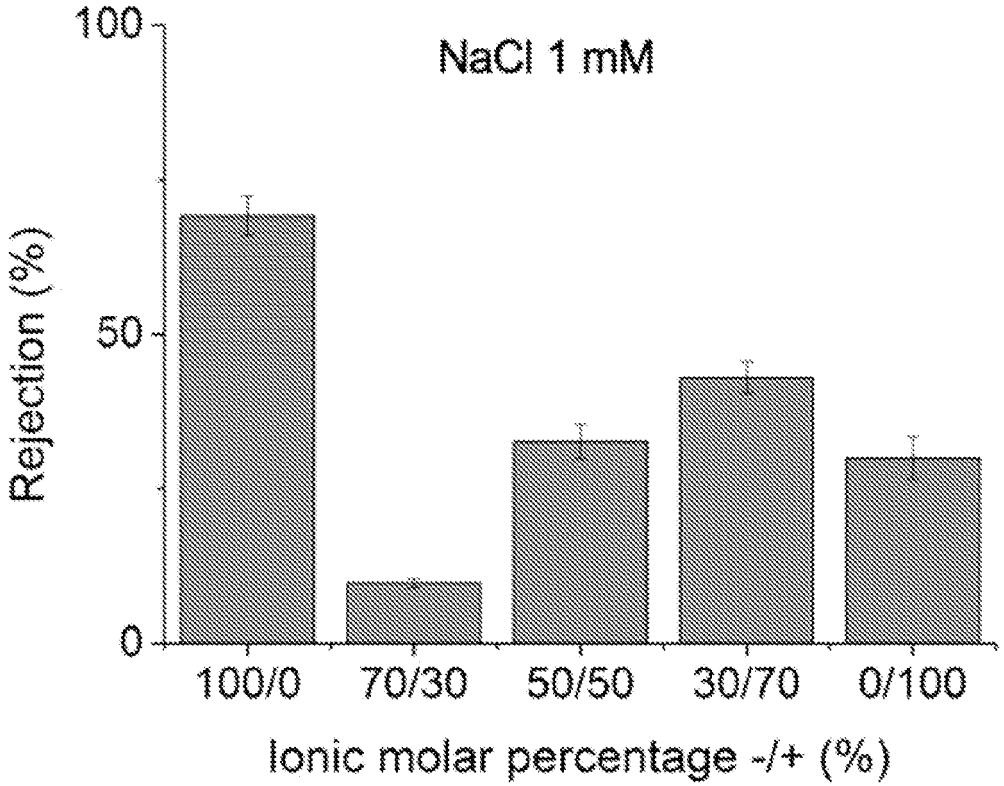

100
50
0
Rejection (%)
$MgCl_2$ 1 mM
$MgCl_2$ 10 mM
100/0
70/30
50/50
30/70
0/100
Ionic molar percentage -/+ (%)

FIG. 23


NaCl 1 mM
Rejection (%)
100
50
0
100/0
70/30
50/50
30/70
0/100
Ionic molar percentage -/+ (%)

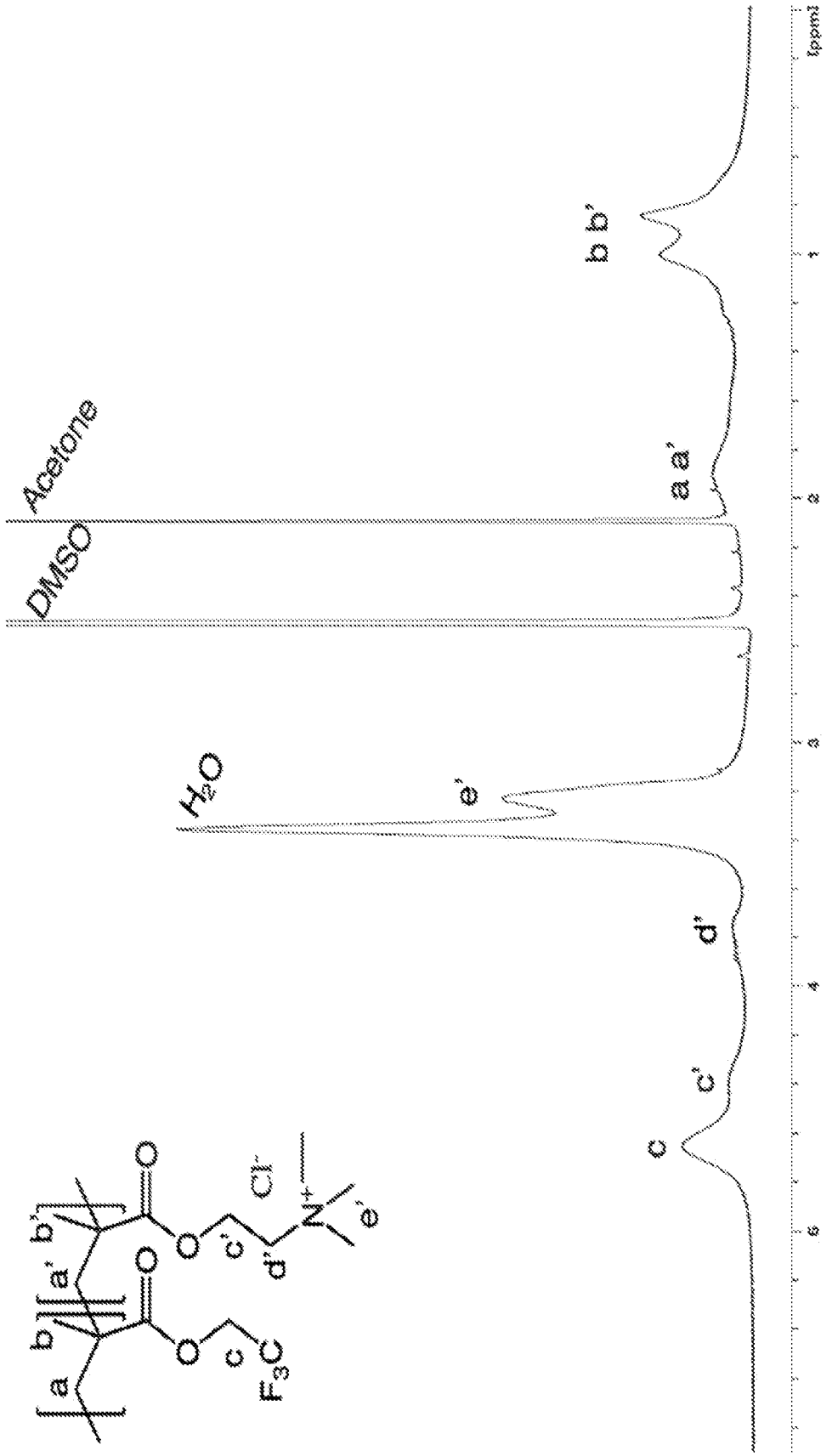


FIG. 24

FIG. 25

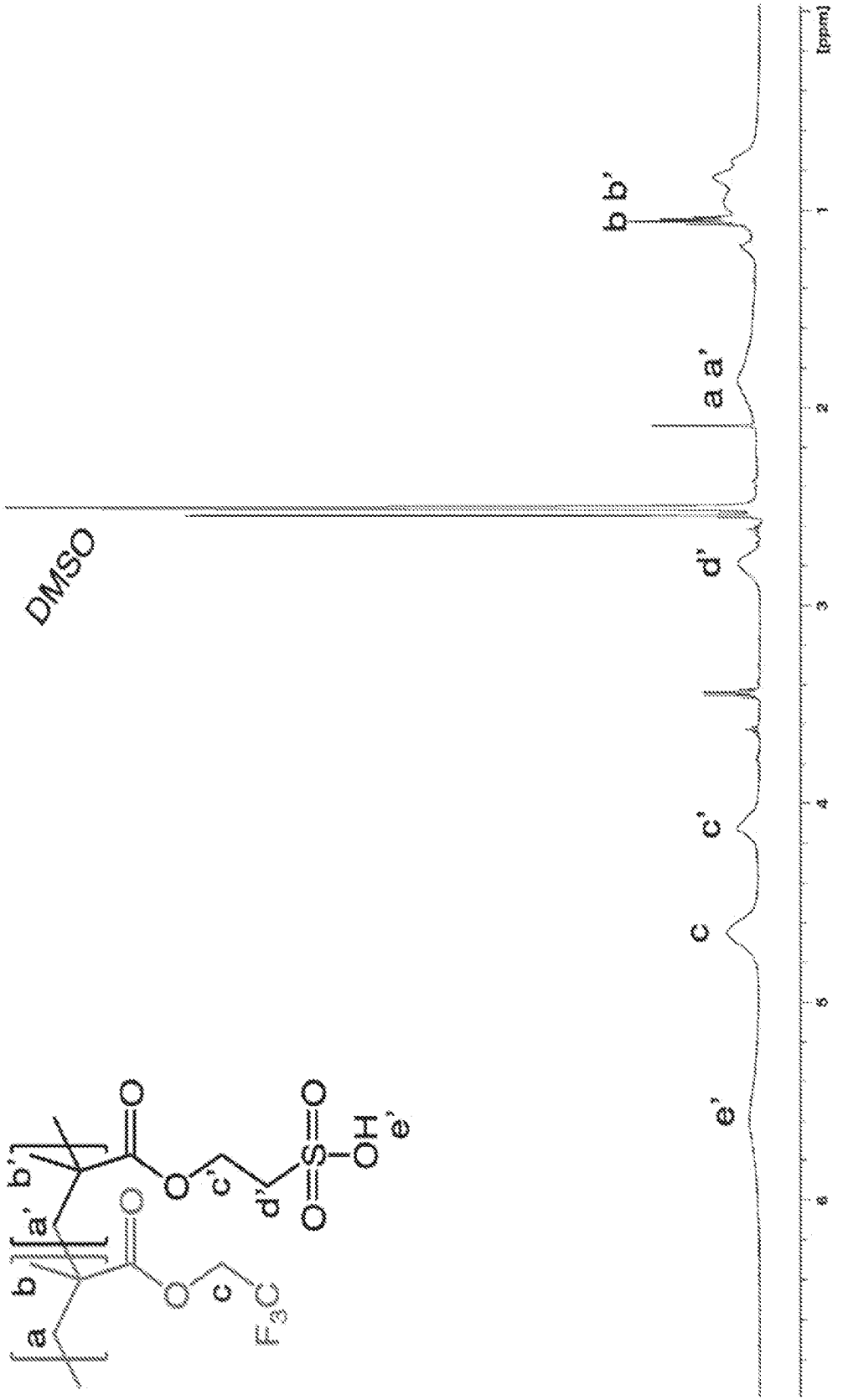


FIG. 26

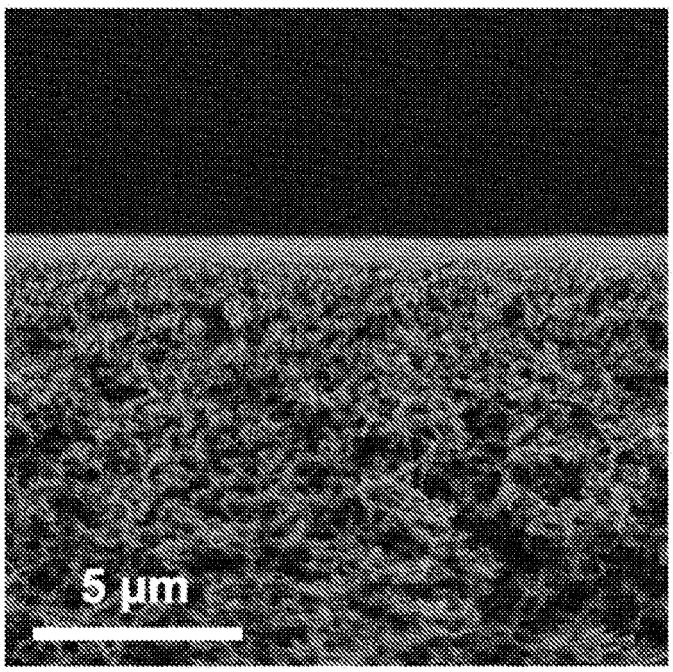


FIG. 27

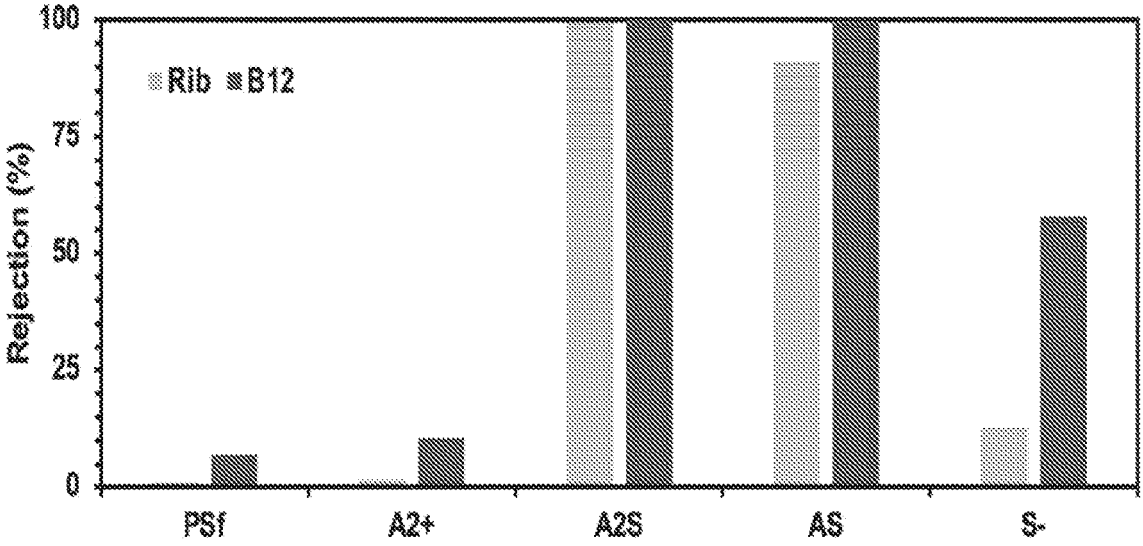


FIG. 28

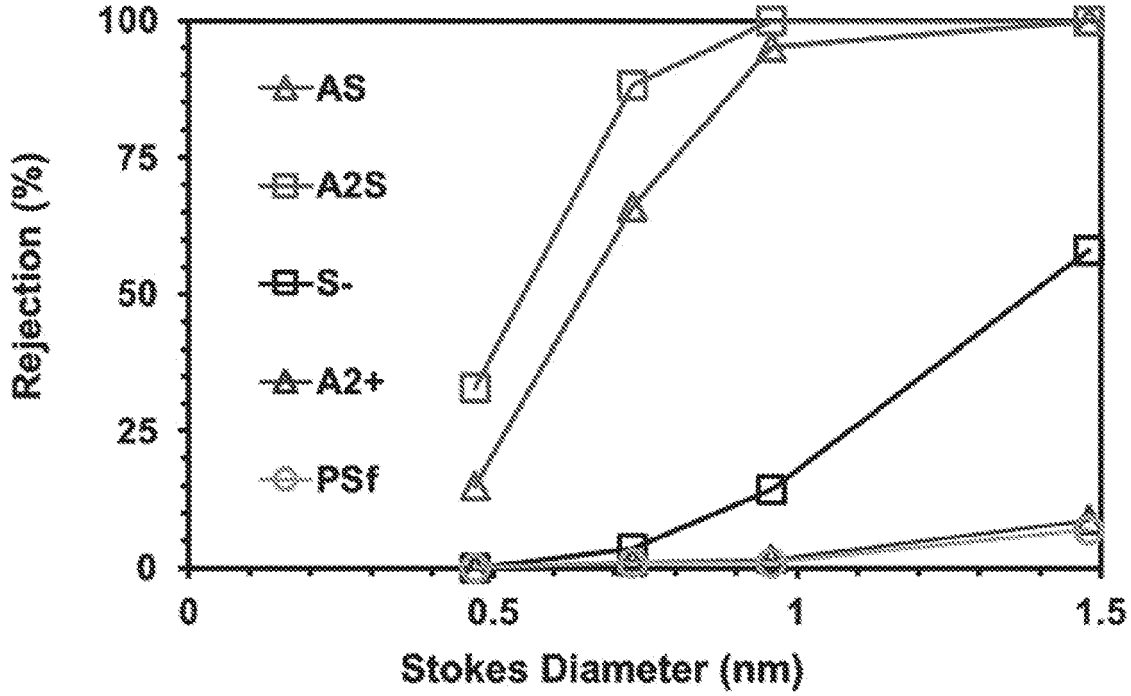

100
75
50
25
0
Rejection (%)
AS
A2S
S-
A2+
PSf
0
0.5
1
1.5
Stokes Diameter (nm)

FIG. 29

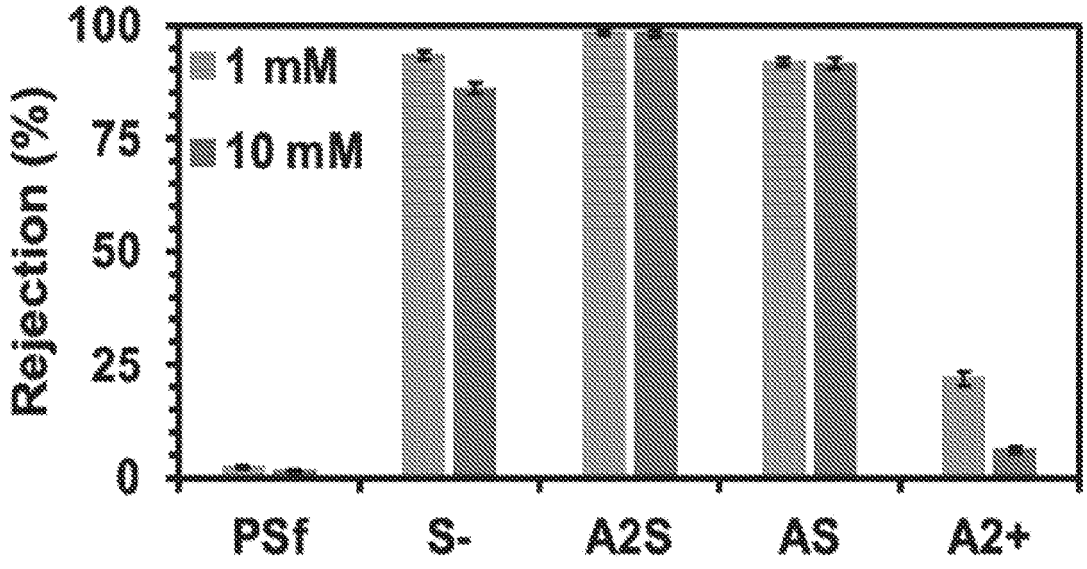

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
A2S
AS
A2+

FIG. 30

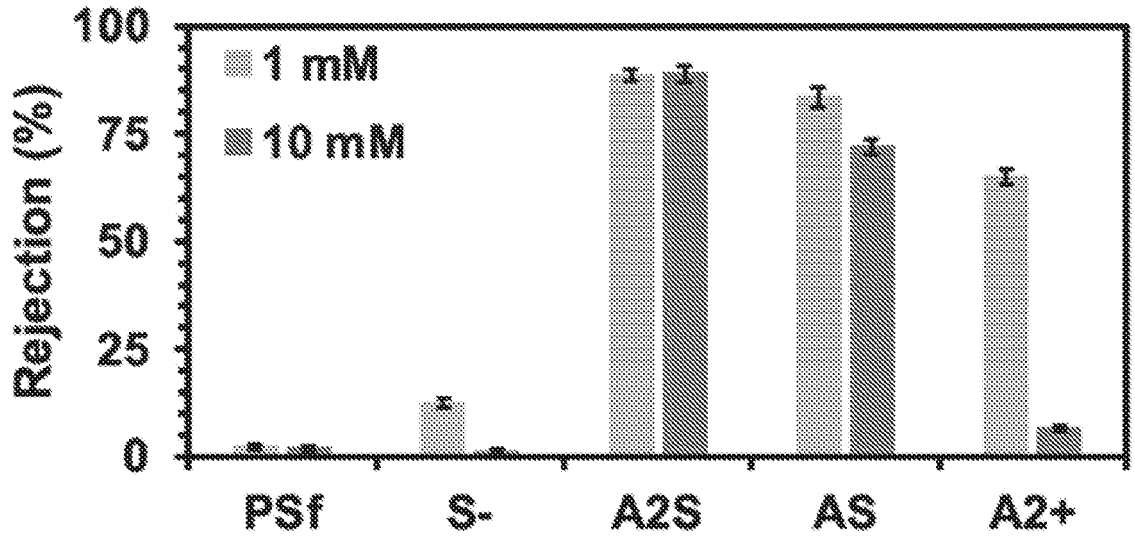
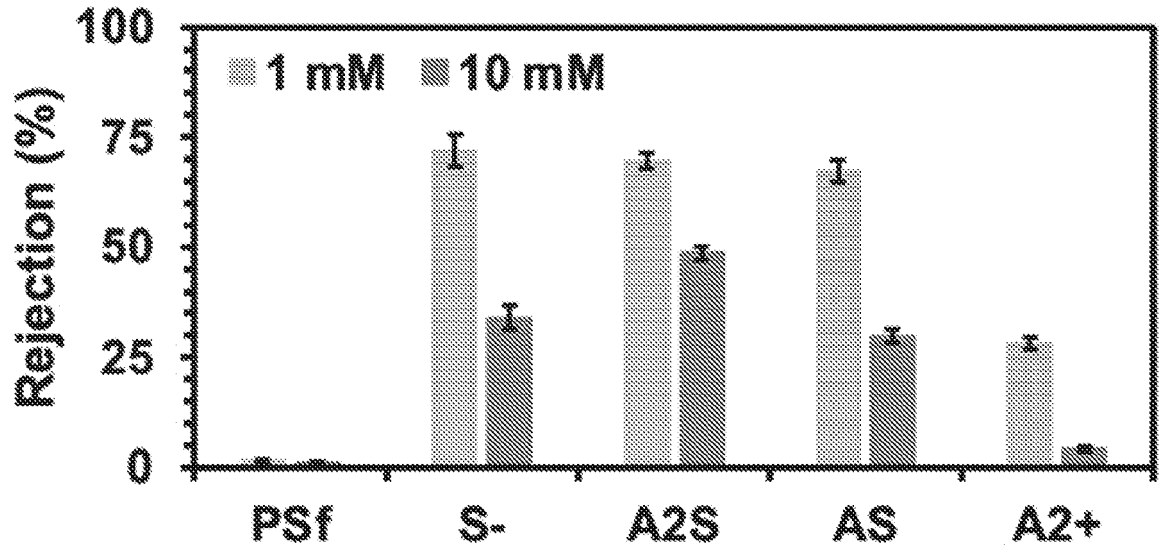

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
A2S
AS
A2+

FIG. 31


100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S-
A2S
AS
A2+

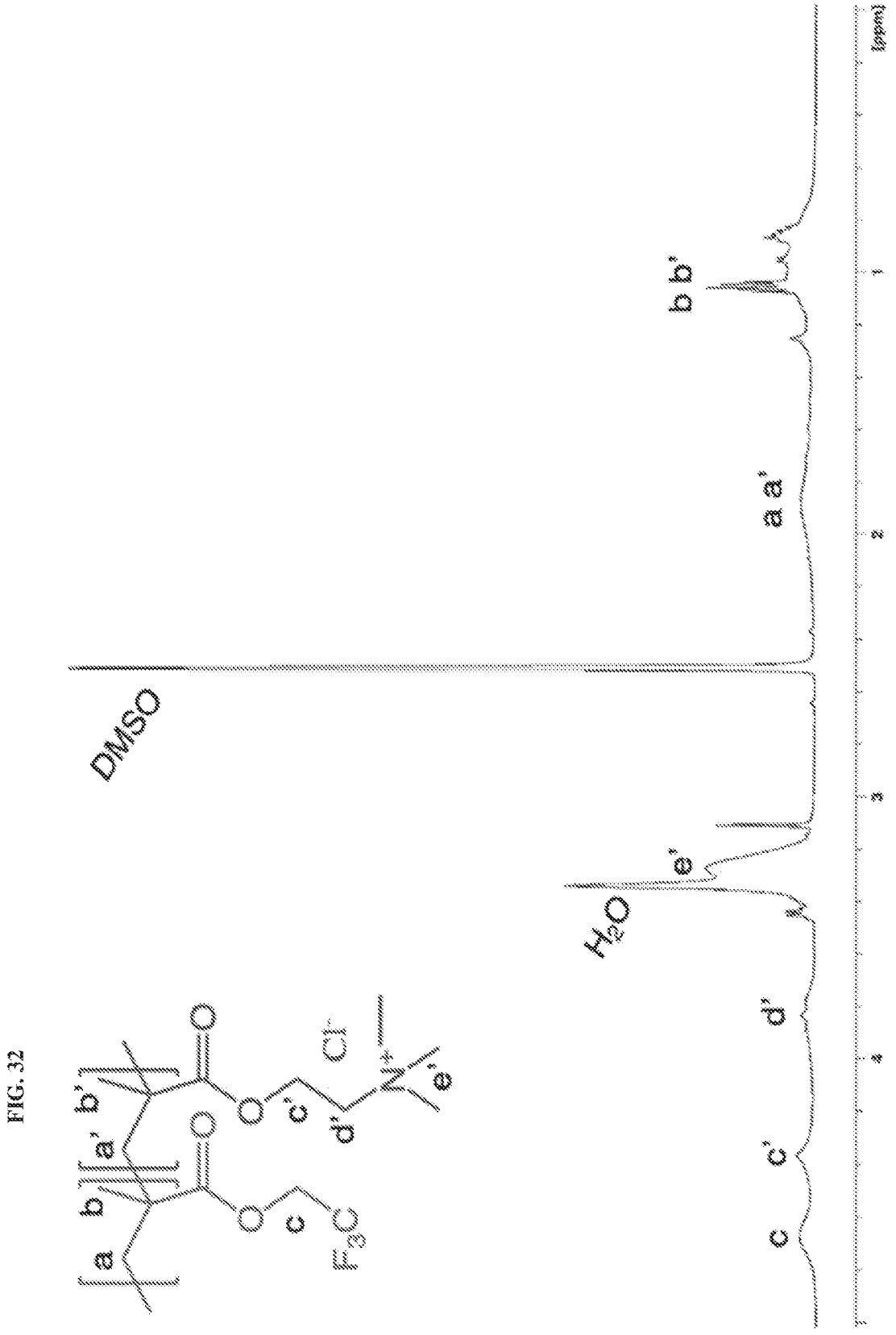


FIG. 32

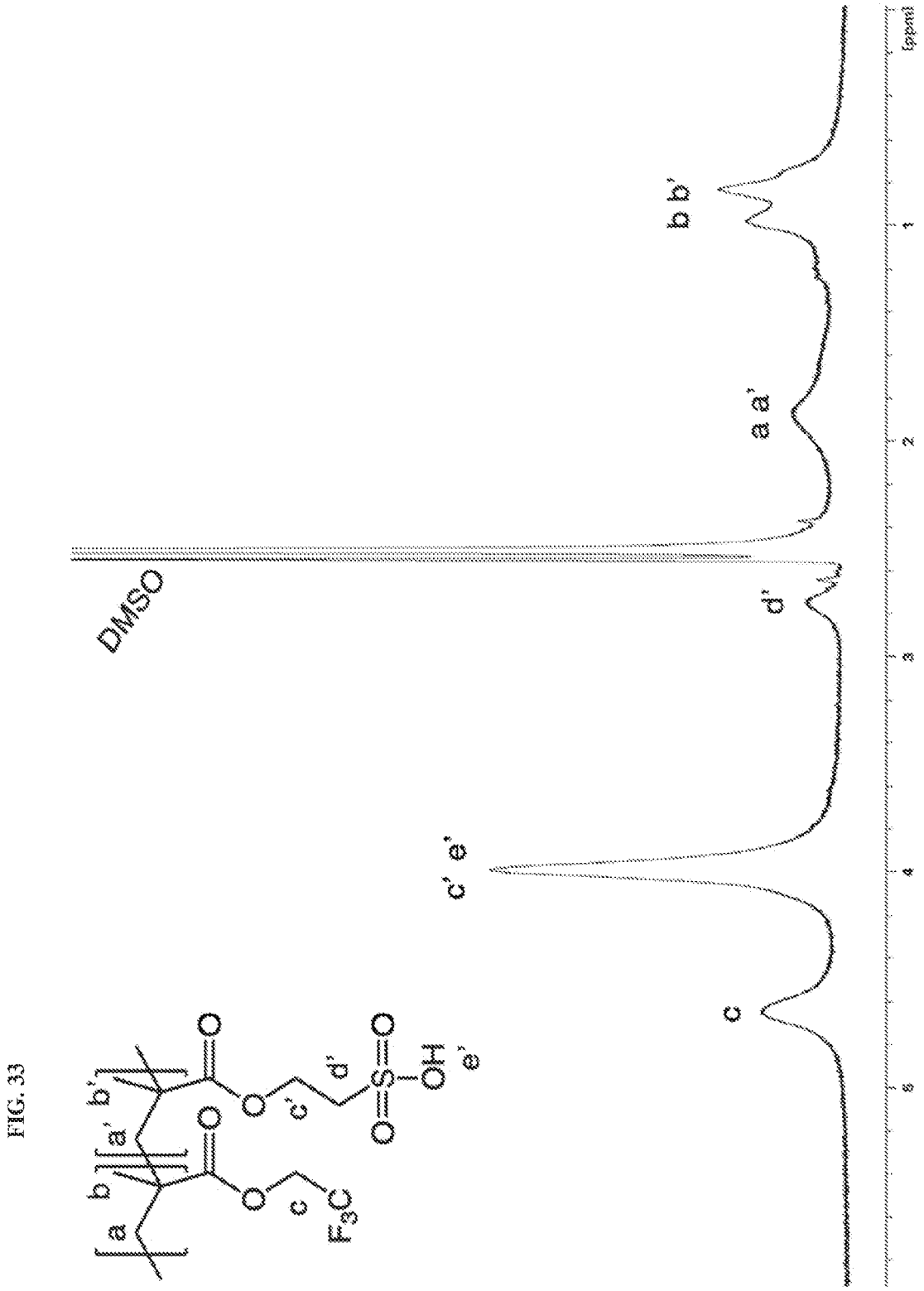


FIG. 33

FIG. 34

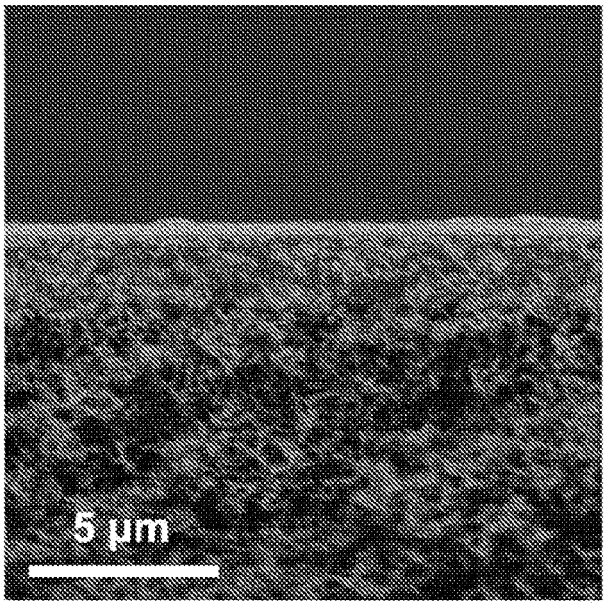


FIG. 35

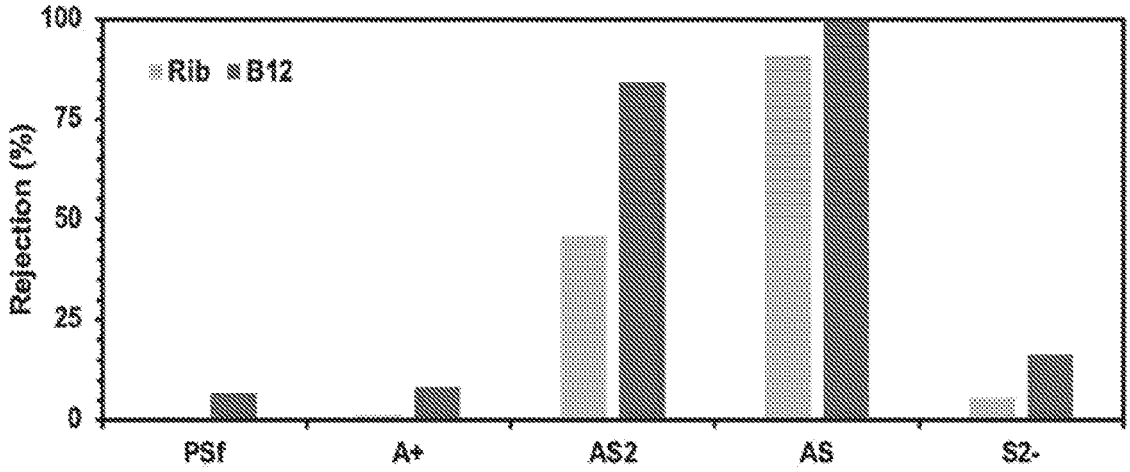


FIG. 36

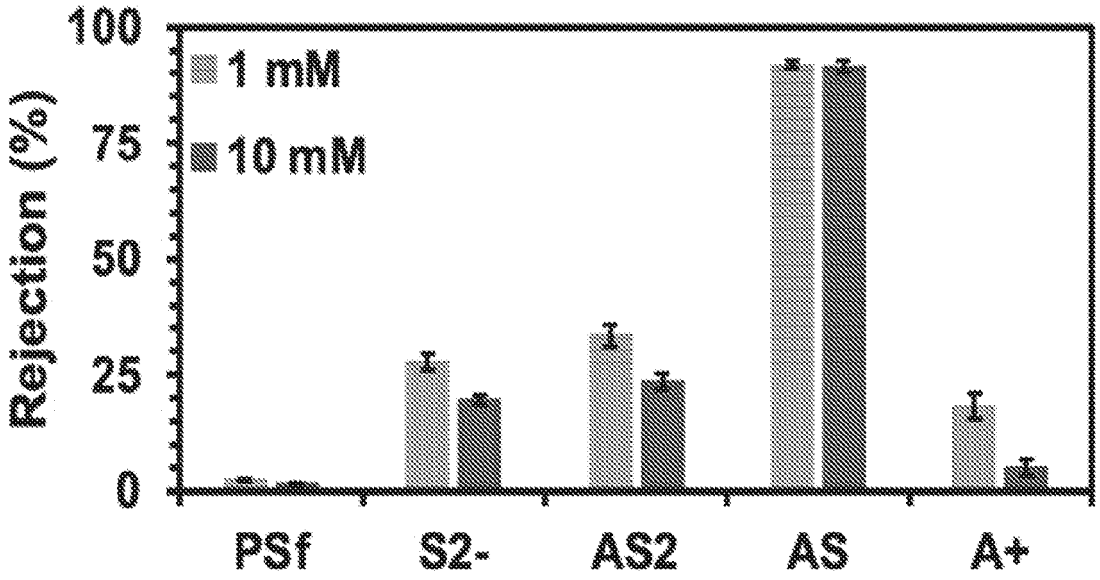


FIG. 37

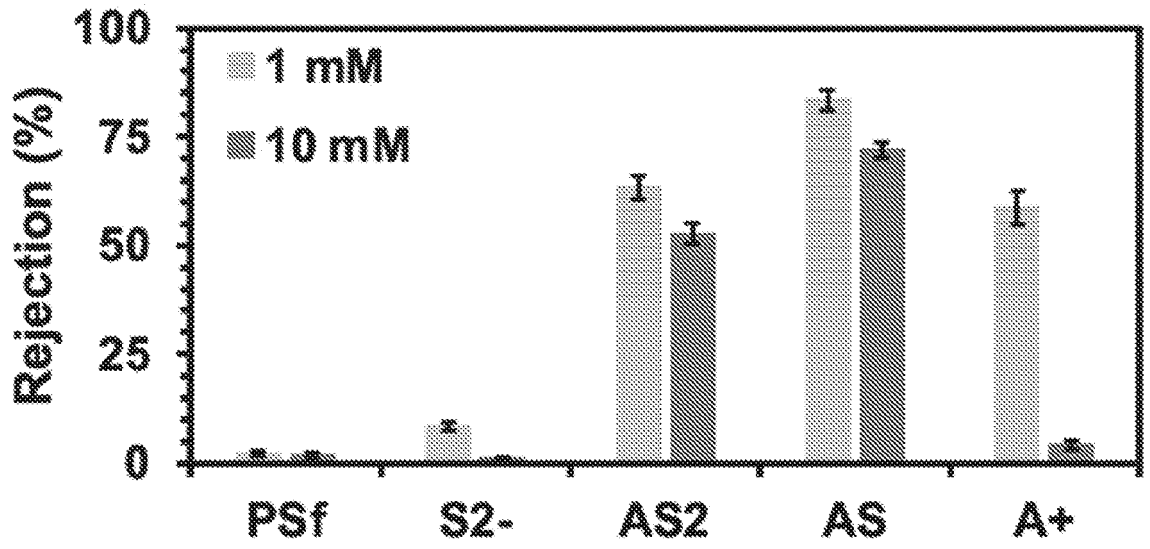
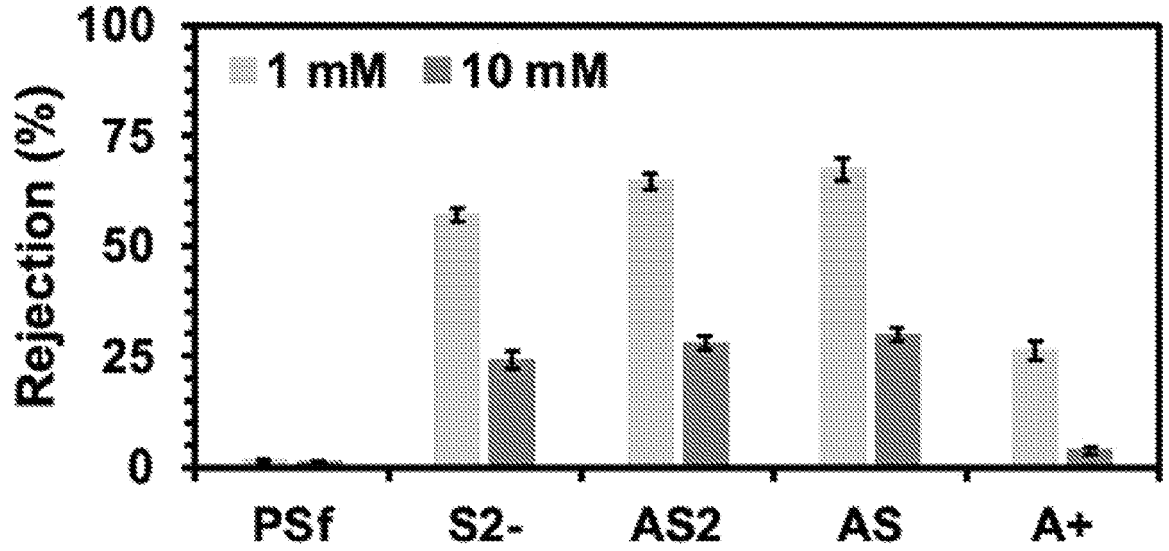

100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S2-
AS2
AS
A+

FIG. 38


100
75
50
25
0
Rejection (%)
1 mM
10 mM
PSf
S2-
AS2
AS
A+