(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 September 2012 (27.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/128939 A2

(51) International Patent Classification:
C08L 33/16 (2006.01)

(21) International Application Number:
PCT/US2012/027935

(22) International Filing Date:
7 March 2012 (07.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/454,201 18 March 2011 (18.03.2011) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2012/128939 A2

(54) **Title**: FLUOROPOLYMER COMPOSITIONS FOR DESALINATION MEMBRANES

(57) **Abstract**: The invention relates to the use of membranes formed from blends of a fluoropolymer matrix with polyelectrolytes and/or compatible hydrophilic polymers. The membranes are useful in water purification, and especially for purification of brackish and high saline content waters. The membranes can provide energy savings in a reverse osmosis (RO) system by requiring less back pressure. The membranes also offer a high degree of chemical resistance, including resistance to sodium hypochlorite, chlorine dioxide and hydrogen peroxide.

FLUOROPOLYMER COMPOSITIONS FOR DESALINATION MEMBRANES

Field of the Invention

The invention relates to the use of membranes formed from blends of a fluoropolymer matrix with polyelectrolytes and/or compatible hydrophilic polymers. The membranes are useful in water purification, and especially for purification of brackish and high saline content waters. The membranes can provide energy savings in a reverse osmosis (RO) system by requiring less back pressure. The membranes also offer a high degree of chemical resistance, including resistance to sodium hypochlorite, chlorine dioxide and hydrogen peroxide.

Background of the Invention

There is a growing need to supply fresh water on a global basis to meet the needs of expanding populations. A variety of membrane technologies are actively employed to meet this need. Microfiltration (MF) and ultrafiltration (UF) are used to purify surface waters for drinking, pre-treat brackish and sea water for reverse osmosis, and treat waste water (especially in membrane bioreactors) prior to discharge into the environment.

Reverse osmosis (RO) is a procedure by which impurities are removed from water using high pressure and specialized membranes. Impure water is pressurized and forced through a composite membrane. The membrane is designed such that it is mechanically strong and preferentially rejects salts and other impurities while allowing water molecules to pass. This practice has found commercial application, particularly in areas where fresh water is in short supply (sea water desalination). The main drawback to RO water purification is that a large amount of energy must be expended to pressurize the water and force it through the membranes. There is a need to develop a membrane that allows water to permeate more readily while maintaining high rejection of impurities would be a major advancement.

Another major limitation of current commercial RO membranes is that they have poor tolerance to chlorine and other oxidants used in water purification. The inability to treat these membranes with chlorine leads to problems with biofilm growth. The biofilm growth greatly reduces pure water flux and system efficiency, which add significant cost to the RO process. It is desired to have a RO membrane with superior chlorine resistant.

Fluoropolymers, and especially polyvinylidene fluoride (PVDF), are preferred polymer materials for MF and UF membranes due to the excellent chemical resistance, especially to oxidants and halogens used in water purification. PVDF is also convenient to process by solution casting (or melt casting) into porous membranes. Since PVDF is a very hydrophobic polymer, it increases resistance to water flux in membranes. It is necessary to modify the PVDF to improve water flux.

Many methods have been described for post treatment of PVDF membranes to decrease the hydrophobicity and increase water flux. These methods typically involved treating a porous PVDF membrane with a hydrophilic monomer (e.g. acrylic acid or hydroxyethylmethacrylate) followed by polymerization to create a hydrophilic surface treatment. These methods are described in US 4618533 (M.J. Steuck inventor, 10/21/86), US 4855163 (I.B. Joffe, P.J. Degen, F.A. Baltusis inventors, 8/8/89), and R. Revanur et al *Macromolecules* 2007, *40*, 3624-3620. These polymerizations are typically free radical in nature, initiated either chemically or by radiation.

WO 10/51150, describes blending a hydrophobic matrix polymer (such as PVDF) with compatible amphiphilic block copolymers to increase the water flux.

Fuel cell membranes have been formed from various polyelectrolytes blended with poly(vinylidene fluoride), poly(vinylidene fluoride) copolymers, and potentially other matrix copolymers. These polymer blends exhibit physical, chemical, electrochemical, and transport properties characteristic of both the PVDF and the polyelectrolyte components. Films of these polymer blends have been optimized for use in hydrogen fuel cells. US 7,449,111; US 7,396,880; USSN 12/519072; and US2006/0014067. These references are incorporated herein by reference.

It has now been found that a membrane formed from a compatible blend of a fluoropolymer matrix with a polymer having some hydrophilic activity (either a polyelectrolyte or a hydrophilic polymer), is useful in water purification, especially for brackish water or water having a high saline content. The membrane has excellent chemical resistance, including to sodium hypochlorite, chlorine dioxide, and hydrogen peroxide. A preferred fluoropolymer matrix is a fluoropolymer having vinylidene fluoride units.

Summary of the Invention

The invention relates to a dense polymer membrane comprising:

a) 99-20 weight percent of a hydrophobic matrix polymer; and

b) 1-90 weight percent of a hydrophilic polymer,

where the hydrophobic matrix polymer and the hydrophilic copolymer are compatible, and wherein said dense polymer membrane has a maximum pore size of 0.05 microns or less.

Detailed Description of the Invention

Unless stated otherwise, all percentages, parts, ratios, etc. are by weight, and molecular weights are weight average molecular weight. All references cited are incorporated herein by reference.

The present invention relates to a membrane made from a blend of a fluoropolymer and a compatible hydrophilic polymer, the blend being useful in water purification. The hydrophilic compatible polymer may be either a polyelectrolyte, or a polymer having hydrophilic activity. The hydrophilic polymer may be a homopolymer or copolymer. A preferred copolymer is a block copolymer, especially an amphiphilic copolymer containing a hydrophobic matrix compatible block and a matrix incompatible hydrophilic block. The matrix polymer is a tough, and highly chemical-resistant (co)polymer, preferably a fluoropolymer.

By "compatible" as used herein is meant that the blend (in the melt or solution) of the matrix polymer and hydrophilic polymer does not exhibit any visual morphological macrophase separation when formed into films or membranes by a cast or solution process. By visual macrophase separation is meant that individual phases are less than 30 microns, and preferably less than 20 microns, and even less than 15 microns and less than 5 microns in average diameter.

By "copolymer" as used herein in meant a polymer formed from two or more monomers, including terpolymers and polymers having more than three polymer units. The copolymers may be graft copolymers. The copolymers may have any polymer architecture, including, but not limited to: random, block, tapered, star, comb copolymers.

Matrix

The membrane matrix polymer can be any hydrophobic polymer. Fluoropolymers are preferred and polymers containing a majority of vinylidene fluoride monomer units are most preferred. Fluoropolymers, as used in the invention are those containing at least 50 mole percent of one or more fluoromonomers. Useful hydrophobic monomers include, but are not limited to, PVDF, PVDF copolymers, PVDF-co-hexafluoropropylene (HFP), ECTFE, polyvinylfluoride, polytetrafluroethylene (PTFE), polyvinyl chloride (PVC), polyolefins, polystyrene (and styrene derivatives), polysulfones, polyethersulfones, the copolymers/terpolymers of these polymers, and blends thereof.

Fluoromonomers useful in the practice of the invention include, for example, vinylidene fluoride (VF_2), tetrafluoroethylene (TFE), trifluoroethylene, chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), vinyl fluoride, hexafluoroisobutylene, 1234yf (tetrafluoro propylene, perfluorobutylethylene (PFBE), pentafluoropropene, 3,3,3-trifluoro-1-propene, 2-trifluoromethyl-3,3,3-trifluoropropene a fluorinated vinyl ether, a fluorinated allyl ether, a non-fluorinated allyl ether, a fluorinated dioxole, and combinations thereof.

Especially preferred copolymers made by the process of the invention are copolymers of VDF with HFP, TFE or CTFE, comprising from about 50 to about 99 weight percent VDF, more preferably from about 70 to about 99 weight percent VDF. Especially preferred terpolymers are the terpolymer of VDF, HFP and TFE, and the terpolymer of VDF, trifluoroethene, and TFE. The especially preferred terpolymers have at least 10 weight percent VDF, and the other comonomers may be present in varying portions, but together they comprise up to 90 weight percent of the terpolymer.

Polyelectrolytes

In one embodiment, the matrix polymer is blended with one or more polyelectrolye (co)polymers. The polyelectrolyte copolymer contains ionic or ionizable groups, and may contain groups capable of crosslinking. The polyelectrolyte contains at least one ionic or ionizable group, such as sulfonate, phosphonate or carboxylate groups. The level of monomer units containing ionic or ionizable groups should be high, preferably from 25 to 99 weight percent, more preferably from 50 to 95 weight percent, and most preferably from 70 to 95 weight

percent in the polyelectrolyte. The ionic or ionizable groups may be present on the monomer used to form the polyelectrolyte, or may be added to the polyelectrolyte in a post-polymerization reaction.

In one preferred embodiment, the polyelectrolyte resins have good chemical resistance, such as (co)polymer resins without hydrolyzable groups.

The polyelectrolyte may be non-perfluorinated, partially-perfluorinated or entirely perfluorinated (co)polymers. The level of perfluorination can have dramatic effects on the ionic conductivity, mechanical strength, and permeability of the resultant (co)polymer blend(s).

The polyelectrolyte can be formed by emulsion, suspension, inverse emulsion, or solution polymerization. It may also be formed by a post-polymerization modification. The polymerization may be traditional copolymerization involving two separate monomers, or the formation of a copolymer based on partial reaction(s) of a homopolymers to form two or more separate functional monomer units.

Examples of vinyl monomers that can be used in the polyelectrolyte backbone include, but are not limited to, styrene, vinyl acetate, vinyl ethers, vinyl esters such as VeoVa 9 and VeoVa 10 from Shell, vinyl propionate, vinyl pivalate, vinyl benzoate, vinyl stearate, and the like, and any combinations thereof.

Examples of aromatic polylelectrolytes include, but are not limited to, the sulfonated or phosphinated forms of poly(ether ether ketone), poly(ether ketone ketone), and poly(phenylene sulfide).

Furthermore, the polyelectrolyte contains at least one ionic (e.g., sulfonate or phosphonate) or ionizable group such as a sulfonated or phosphonated group or sulfonyl groups. An ionizable group is a group capable of forming an ionic group, such as cyclic amino acids, sultones, maleic anhydride, mercaptans, sulfides, phosphalanes, and the like. These groups can be part of the non-perfluorinated polyelectrolyte by any means such as blending an acrylic and/or vinylic resin in the presence of one or more monomers containing an ionic or ionizable group. In the alternative, one or more of the monomers used to form the non-perfluorinated polyelectrolyte can contain the ionic or ionizable group.

With respect to the acrylic resin or polymer, this polymer or resin preferably contains or bears one or more ionic or ionizable groups. Examples of acrylic resins include polymers (including copolymers, terpolymers, oligomers, and the like) of acrylic acids, methacrylic acids, esters of these acids, or acrylonitrile. The acrylic

resin can also contain other repeating units as well as combinations of different acrylic acid alkyl esters, methacrylic acid alkyl esters, acrylic acids, methacrylic acids, and acrylonitriles. For purposes of the present invention, the acrylic resin can include other polymerized monomers or can be a mixture of two or more different acrylic resins or can additionally include non-acrylic resins, such vinyl monomers and styrenic monomers.

Besides the components mentioned above with respect to the acrylic and/or vinylic resin, the acrylic and/or vinylic resin can further contain or be formed in the additional presence of one or more additional monomers optionally with any type of functional group as long as these monomers are compatible with the overall formation of the acrylic and/or vinylic resin.

Preferably the acrylic and/or vinylic resin is the result of the polymerization of several monomers, one of which contains the ionic or ionizable group, and the other which contains the acrylic and/or vinylic units of the acrylic and/or vinylic resin. More preferably, the acrylic and/or vinylic resin is formed from polymerizing (1) acrylic acid alkyl esters, (2) methacrylic acid alkyl esters, (3) one or more co-polymerizable monomers which are different from (1) and (2), (4) one or more monomers having at least one functional group, (5) a monomer containing ionic or ionizable groups, such as a sulfonated or phosphonated monomer.

Examples of the acrylic acid ester (1) include, for example, ethyl acrylate, methyl acrylate, butyl acrylate, propyl acrylate, isobutyl acrylate, amyl acrylate, 2-ethylhexyl acrylate, hexyl acrylate, fluoroalkyl acrylates, and combinations thereof.

Examples of the methacrylic acid ester (2) include, for example, ethyl methacrylate, methyl methacrylate, butyl methacrylate, propyl methacrylate, isobutyl methacrylate, amyl methacrylate, 2-ethylhexyl methacrylate, hexyl methacrylate, fluoroalkylmethacrylate, and combinations thereof.

Examples of the functional monomers (3) include, but are not limited to α, β unsaturated carboxylic acids (e.g., acrylic acid, methacrylic acid, fumaric acid, crotonic acid, itaconic acid); vinyl ester compounds, amide compounds (e.g., acrylamide, methacrylamide, N-methylmethacrylamide, N-methylolmethacrylamide, N-alkylacrylamide, N-alkylacryl methamide, N-dialkyl methacrylamide, N-dialkyl acrylamide); monomers containing hydroxyl group (e.g., hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, diethylene glycol ethyl ether acrylate); monomers containing epoxy groups (e.g.,

glycidyl acrylate, glycidyl methacrylate), monomers containing silanols (e.g., γtrimethoxysilane methacrylate, γtriethoxysilane methacrylate); monomer containing aldehydes (e.g., acrolein), alkenyl cyanides (e.g., acrylonitrile, methacrylonitrile). The monomers included in (4) can be capable of crosslinking. Examples of copolymerizable monomers capable of crosslinking include isobutyl methacrylamide, glycidyl methacrylate, diethylene glycol dimethacrylate, and trimethyloxysilane methacrylate. Crosslinking might be desirable for improved mechanical properties and solvent resistance.

Examples of the monomer containing at least one ionic or ionizable group include, but are not limited to, acrylamide propyl sulfonate, vinyl phosphonic acid, vinyl sulfonic acid, sulfopropyl methacrylate, sulfoethyl methacrylate. These monomers can preferably be used either in their acid form or as a salt derivative. For example, in a seeded emulsion polymerization, the sulfonated monomer can be incorporated in either the first stage or the second stage or both stages. The amount of the ionic group is preferably from about 200 to about 2500 EW, and more preferably from about 200 to about 1100 EW, wherein EW is equivalent weight and is the number of grams of polymer per sulfonated unit.

The polymer of the present invention which contains at least one acrylic or vinyl resin or both having at least one ionic or ionizable group preferably has an equivalent weight with respect to the acrylic or vinyl resin of from about 200 to about 4,000 and more preferably from about 200 to about 1,400. This preferred equivalent range provides preferred properties with respect to membrane formation and the ability to avoid the need for fluoropolymers. The polymer of the present invention can optionally be formed as a blend. Preferably, the polymer of the present invention is crosslinked using conventional crosslinking techniques.

Crosslinking can be done via conventional methods including, but not limited to, self-condensation, addition of a secondary crosslinker, or radiation crosslinking. These are well described in the literature and well known in the art. Examples of monomers able to undergo self-condensation crosslinking include N-methylol acrylamide, isobutoxy methacrylamide, N-methylenebisacrylamide, and glycidyl methacrylate. Examples of secondary crosslinkers include isocyanates, melamines, epoxies, carboxylates, alkoxy silanes, silicones, aziridines, and carbodiimides. Examples of radiation crosslinking include electron beam, ultraviolet, and gamma

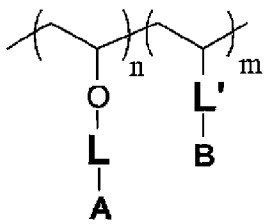
radiation.

The polymerization of the mixture of polymerizable vinyl, acrylic and/or aromatic containing monomers can be carried out separately and then blended with one or more polymer(s), or polymerized in the presence of one or more polymers. The polymerization monomers can be prepared by solution, bulk, emulsion polymerizations, or any other known polymerization methods.

The level of cross-linking moieties is from 1-75 weight percent, preferably 1-50 weight percent, more preferably from 10-30 weight percent, and most preferably from 10-20 weight percent, based on the weight of the copolymer. Cross-linking can be done via conventional methods including, but not limited to, self-condensation, addition of a secondary cross-linking agent, or radiation crosslinking. These are well described in the literature and well known in the art. Examples of monomers able to undergo self-condensation crosslinking include, but are not limited to: primary, secondary, and tertiary amines; N-methylol acrylamide; isobutoxy methacrylamide; N-methylenebisacrylamide; allyl groups, styryl groups; and glycidyl methacrylate. Examples of secondary cross-linkers include free and blocked isocyanates, melamines, epoxies, carboxylates, α,ω-dihaloalkanes, α,ω-dialdehydes, carboxylic acids, alkoxy silanes, silicones, aziridines, and carbodiimides. Catalysts can be chosen for the specific crosslinking chemistry and would include organotins, sulfonic acids, or amines. Examples of radiation cross-linking include electron beam, ultraviolet, and gamma radiation.

The polyelectrolytes of the invention include, but are not limited to vinyl ether-type polyelectrolytes, styrenic-type polyelectrolytes and polyelectrolytes having backbone aromatic groups.

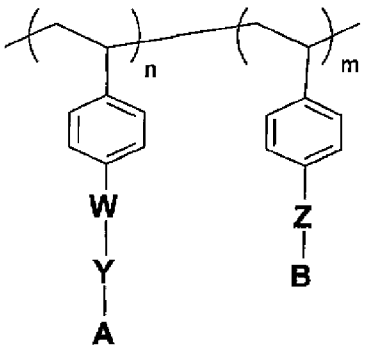
The general structure of vinyl-ether-type polyelectrolyte structures of the present invention is:



Where:
L = non-perfluorinated alkyl or alkylene-etheralkylene-ether linkage

L' = a bond or alkyl or alkylene-etheralkylene-ether linkage
n = 25-99 mol%, preferably greater than 50%, most preferably greater than 70%
m = 1-75 mol%, preferably less than 50%, most preferably less than 30%
A = a sulfonate, phosphonate or carboxylate
B = a group capable of cross-linking

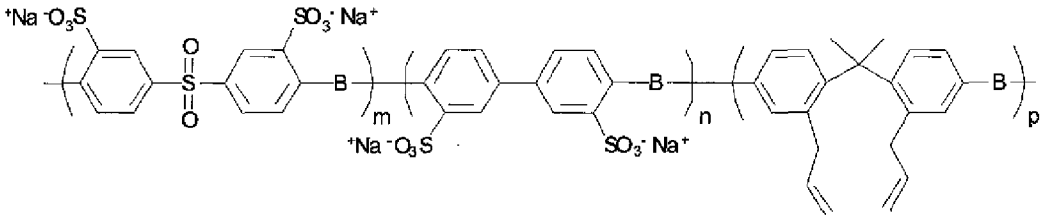
The general structure of styrenic-type polyelectrolyte structures of the present invention is:



Where:
W = a bond, O, NH, S, SO, or SO_2
Y = alkyl, aromatic, or alkylene-etheralkylene-ether linkage of C_1 to C_{12} [eg. $(-CH_2-)_{1-12}$]
Z = a bond, alkyl, aromatic,or alkylene-etheralkylene-ether linkage of C_1 to C_{12}
n = 1-99 mol%, preferably greater than 50%, most preferably greater than 70%
m = 1-99 mol%, preferably less than 50%, most preferably less than 30%
A = a sulfonate, phosphonate or carboxylate
B = a group capable of cross-linking

Based on the general structure above, one can envision many routes to these types of copolymers including, but not limited to (co)polymerization of the pre-functionalized monomers, and post-polymerization modification of appropriately-functionalized polystyrenics. Some of the most preferred routes to these copolymers are outlined below.

Polyelectrolytes having one or more backbone units where the polyelectrolyte backbone contains substituted aryl units and no linear alkyl units of 2 or more carbons in the backbone, and where the aryl groups are substituted from 0 to about 100 mole percent of highly-acidic functional groups and/or from 0 to about 100 mole percent of cross-linkable groups and where the aryl groups are joined together by electron-withdrawing and/or nucleophilic functional groups. An example of this type of polyelectrolyte would be of the formula:



wherein:
n = (1-m)-p
p = (1-m)-n
m = 0.5 (50 mol.-% of monomer units)
n = 0.01 to 0.49 (1 mol.-% to 49 mol.-% of monomer units)
p = 0.01 to 0.49 (1 mol.-% to 49 mol.-% of monomer units).

Polyelectrolytes of the invention also includes sulfonated polyether ketone ketone
(PEKK), and sulfonated polyether ether ketone (PEEK).

Hydrophilic polymers

In another embodiment, the matrix polymer is blended with one or more hydrophilic polymers. A hydrophilic polymer of the invention is one having hydrophilic acivity. The hydrophilic activity can be due to hydrophilic functionality in monomer units in the polymer beakbone, or the hydrophilically active groups may be grafted onto the polymer backbone. Some portion of the hydrophilic polymer must be compatible enough with the matrix polymer to provide good dispersion without macrophase separation. The hydrophilic polymer may be a homopolymer or copolymer. Some useful hydrophilic polymers include, but are not limited to polyvinylpyrrolidone (PVP), and copolymers, block copolymers and ionomers of PVP (such as PVP-polyvinyl acetate).

Acrylic copolymers having hydrophilic comonomers are also included in the invention. . By "hydrophilic monomer" is meant any polymerizable monomer with a solubility of at least 6 grams of monomer per 100 grams of water, preferably with a solubility of at least 10 grams of monomer per 100 grams of water. Hydrophilic monomers useful in the invention include hydroxy alkyl (meth) acrylates, (meth)acrylic acid, (meth)acrylic amides, (meth)acrylic amines. Examples of hydrophilic monomners include, but are not limited to 2-hydroxylethyl methacrylate, 2-hydroxylethyl acrylate, methacrylic acid, acrylic acid, hydroxypropyl methacrylate, 4-hydroxybutylacrylate, ethyl alpha-hydroxymethacrylate, allyl cellosolve, allyl

carbinol, methylvinyl carbinol, allyl alcohol, methyllyl alcohol, glycidyl methacrylate, 3,4-epoxybutyl acrylate, acrylonitrile, methacrylonitrile, beta-cyanoethyl methacrylate, beta-cyanoethyl acrylate, cyanoalkoxyalkyl (meth)acrylates, such as omega-cyanoethoxyethyl acrylate, or omega-cyanoethoxyethyl methacrylate, (meth)acrylamides, such as methacrylamide or acrylamide, N-monoalkyl (meth)acrylamides, such as N-methylacrylamide or N-t-butylacrylamide or N-ethyl (meth)acrylamide, or vinyl monomers containing an aromatic ring and an hydroxyl group, such as vinylphenol, para-vinylbenzyl alcohol, meta-vinylphenethyl alcohol, vinyl pyrrolidone, and vinyl imidazole. The hydrophilic monomer may be copolymerized at about 0.5 to 30 weight percent with hydrophobic acrylic monomers, such as methylmethacrylate, and other C_{1-14} alkyl(meth)acrylates.

In one embodiment the hydrophilic polymer is a block copolymer, and one preferred type of block copolymer of the invention is an amphiphilic block copolymer.

By "block copolymer" as used herein means any controlled-architecture copolymer, including but not limited to true block polymers, which could be di-blocks, tri-blocks, or multi-blocks; branched block copolymers, also known as linear star polymers; comb; and gradient polymers. One or more of the block copolymer segments may contain a graft copolymer. Gradient polymers are linear polymers whose composition changes gradually along the polymer chains, potentially ranging from a random to a block-like structure. Each block of the block copolymers may itself be a homopolymer, a random copolymer, a random terpolymer, a random tetrapolymer, a graft copolymer or a gradient polymer.

By "amphiphilic" as used herein means that at least one block of the copolymer is hydrophilic, and at least one block is hydrophobic.

By "hydrophilic" or "hydrophilic block" as used herein is meant the polymer (or block or segment) is water soluble, water dispersible, or generally capable of absorbing and/or transmitting water. The hydrophilic block could be a hydrophilic homopolymer, a random copolymer containing one or more hydrophilic monomers, or a random copolymer containing one or more hydrophilic monomers with one or more hydrophobic monomers. Ethylenically unsaturated monomers useful in forming the hydrophilic block polymer include but are not limited to, acrylic acid, methacrylic acid, and the salts, esters, anhydrides and amides of methacrylic and acrylic acid; dicarboxylic acid anhydrides; carboxyethyl acrylate; hydrophilic derivatives of

acrylates; hydrophilic derivatives of styrene; and acrylamides. Specific useful monomers include, but are not limited to maleic anhydride, maleic acid, substituted maleic anhydride, mono-ester of maleic anhydride, itaconic anhydride, itaconic acid, substituted itaconic anhydride, monoester of itaconic acid, fumaric acid, fumaric anhydride, fumaric acid, substituted fumaric anhydride, monoester of fumaric acid, crotonic acid and its derivatives, acrylic acid, methacrylic acid, dimethylacrylamide, diethyl acrylamide, n-isopropylacrylamide, dimethylaminoethyl acrylate, diethylaminoethylacrylate, styrene sulfonic acid, acrylamido 2-methyl 2-propane sulfonate, vinylpyrrolidone, 2-carboxyethyl acrylate, methyl acrylate, ethyl acrylate, 2-methoxyethyl acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, polyethylene glycol acrylate, polyethylene glycol methacrylate, polyethyleneglcycol-methylether-acrylate, polyethyleneglycol-methylether methacrylate. Salts of the acid monomers and quaternized versions of the amines are also anticipated in the invention, and the hydrophilic polymer segment may exist in a neutralized or partially neutralized form. Preferred hydrophilic monomers of the invention include acrylic acid (AA), methacrylic acid (MAA), salts of acrylic and methacrylic acid, methoxyethyl acrylate, dimethylacrlyamide, vinylpyrrolidone, 2-carboxyethyl acrylate, polyethylene glycol acrylate (PEGA), polyethyeleneglycol-methylether acrylate (MPEGA), polyethylene glycol methacrylate (PEGMA), polyethyleneglycol-methylether-methacrylate (MPEGMA), and itaconic acid.

The number average molecular weight of the hydrophilic block is in the range of 1 kg/mol to 160 kg/mol, preferably 10 kg/mol to 120 kg/mol, and most preferably 15-100 kg/mol.

The hydrophobic block copolymer segments are hydrophobic homopolymers, random copolymers containing one or more hydrophobic monomers, or a random copolymer containing one or more hydrophobic monomers with one or more hydrophilic monomers. The hydrophobic block is selected for compatibility with the membrane matrix polymer(s). By "hydrophobic" and "hydrophobic polymer" as used herein is meant the polymer block segment is non-soluble or dispersible in water. Examples of ethylenically unsaturated monomers useful in forming the hydrophobic polymer block(s) include, but are not limited to, styrene, hydrophobic derivatives of styrene, conjugated dienes, C_{3-30} straight, cyclic, or branched alkyl and aryl acrylates, C_{1-30} straight, cyclic, or branched alkyl and aryl methacrylates, olefins, fluorine-containing monomers, and silicon-containing monomers. Specific examples of the

hydrophobic monomers include styrene; alpha-methyl styrene, lauryl methacrylate (or other long chain alkyl acrylates or methacrylates, e.g., C_6 –C_{30} alkyl esters 2-ethylhexyl acrylate and 2-ethylhexylmethacrylate, octyl acrylate, and octyl methacrylate, decyl acrylate and decyl methacrylate, etc.), 1,1-dihydroperfluoroalkyl acrylates and methacrylates of the general structure, $CF_3(CF_2)_nCH_2OCOC(R)=CH_2$, in which R is hydrogen or methyl and n is typically 2 to 20, hexafluorobutyl acrylate, triisopropylsilyl acrylate, polydimethylsiloxane acrylate and (meth)acrylate, isobornyl acrylate, isobornyl methacrylate, butadiene, isoprene, methylmethacrylate, *t*-butyl acrylate and *t*-butyl methacrylate. Preferred monomers include, styrene, isobornyl acrylate, isobornyl methacrylate, a mixture of 1,1-dihydroperfluoroalkyl acrylates and methacrylates of the general structure, $CF_3(CF_2)_nCH_2OCOC(R)=CH_2$, in which R is hydrogen or methyl and n is typically 6 to 18, t-butyl acrylate, t-butyl methacrylate and methyl methacrylate.

The number average molecular weight of each end blocks is in the range of 0.5 kg/mol to 120 kg/mol, preferably 3 kg/mol to 60 kg/mol.

The block copolymers of the present invention are formed by a controlled radical polymerization process. These processes generally combine a typical free-radical initiator with a compound to control the polymerization process and produce polymers of a specific composition, specific architecture, and having a controlled molecular weight and narrow molecular weight range. These free-radical initiators used may be those known in the art, including, but not limited to peroxy compounds, peroxides, hydroperoxides and azo compounds that decompose thermally to provide free radicals. In one preferred embodiment the initiator may also contain the control agent. The block copolymers made by a controlled radical polymerization (CRP) process enables tailoring of the block structure to optimize blend stability, matrix compatibility, and hydrophilicity enhancement.

When a copolymer segment is synthesized using a CRP technique such as nitroxide-mediated polymerization, it is often termed a gradient or profiled copolymer. This type of copolymer is different than a copolymer obtained by a traditional free radical process. The properties of the copolymer will be dependant on the monomer composition, control agent used, and polymerization conditions. For example, when polymerizing a monomer mix by traditional free radical polymerizations, a statistical copolymer is produced, as the composition of the monomer mix remains static over the lifetime of the growing chain (approximately 1

second). Furthermore, due to the constant production of free radicals throughout the reaction, the composition of the chains will be non-uniform. During a controlled radical polymerization the chains remain active throughout the polymerization step (i.e., the monomer mix is not static over the lifetime of the growing chain), thus the composition of the chains is uniform and is dependant on the corresponding monomer mix with respect to the reaction time. In a preferred embodiment, the hydrophilic copolymer segment of the invention is a profiled, or gradient block copolymer.

Examples of controlled radical polymerization techniques will be evident to those skilled in the art, and include, but are not limited to, atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer polymerization (RAFT), nitroxide-mediated polymerization (NMP), boron-mediated polymerization, and catalytic chain transfer polymerization (CCT). Descriptions and comparisons of these types of polymerizations are described in the ACS Symposium Series 768 entitled *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*, edited by Krzystof Matyjaszewski, American Chemical Society, Washington, D.C., 2000.

In principle, any living or controlled polymerization technique, compatible with the monomer choices, can be utilized to make the block copolymer. One preferred method of controlled radical polymerization is nitroxide-mediated CRP. Nitroxide-mediated CRP is preferred as it allows for the use of a larger variety of monomers in the triblock copolymer, including the use of acrylics and especially acid functional acrylics. The synthesis of a nitroxide-mediated CRP multi-block amphiphilic copolymer of the invention is found in US 2008/0058475, incorporated herein by reference.

The amphiphilic block copolymers of the invention generally have a molecular weight (Mw) in the range of from 10 kg/mol to 400 kg/mol. The amphiphilic copolymer can contain neutralizable monomer units and in some cases these monomer units can be pre-neutralized. By "neutralized" as used herein is meant that the hydrophilic block of the amphiphilic copolymer is fully or partially in the salt form. Neutralization can take place at any point during the polymerization, or as a post-polymerization process, such as, during the formulation, blending, or fabrication of a film, article, or part. The presence of neutralizable monomer units can impart pH dependency within the membrane.

A preferred block copolymer of the invention is one having a hydrophilic segment and at least one polyvinylidene fluoride compatible or miscible segment. A di-block having a hydrophobic block of primarily polymethylmethacrylate (PMMA), connected to a hydrophilic second block containing primarily (meth)acrylic monomer units. The phase separation of the PMMA (hydrophobic) and hydrophilic blocks is a key part of this invention. This specific phase separation enables a stable additive structure (by compatible mixing of the PMMA block with PVDF) and efficient use of the hydrophilic block, as the hydrophilic block will separate from the PVDF matrix and localize on the pore walls of the membrane. This will generate a hydrophilic internal surface that will promote higher water flux. These amphiphilic blocks may also promote the generation of more uniform pore sizes and may aid in the formation of smaller pore sizes based on the small size scale of phase separation inherent to these materials. The maximum pore size will be less than 0.05 microns, preferably less than 0.02 microns, and most preferably less than 0.01 microns. Such a small maximum pore size creates a dense polymeric membrane.

These types of block copolymers can be either diblock (one PMMA block, one hydrophilic block), or triblock (PMMA-hydrophilic block-PMMA; or hydrophilic block - PMMA - hydrophilic block; or some other unique combination of block structures).

Blending Process

The polyelectrolytes and copolyelectrolytes as described above are processed into a polymer blend as described previously in US 7396880. The blending process is begun by first exchanging the acidic, ionizable groups on the polyelectrolyte with an appropriate tetraalkylammonium hydroxide (TAAOH) to form the tetraalkylammonium salt. Tetraalkylphosphonium hydroxides, such as tetrabutylphosphonium hydroxide, may also be used in the process. Ammonium hydroxides having a formula weight of at least 203 g/mol are preferred. Examples of suitable ammonium salts include: tetrapropylammonium, tetrabutylammonium, tetrapentylammonium, and tetrahexylammonium.

A solution of this TAA-neutralized polyelectrolyte may then be solvent-switched to a solvent which may appropriately dissolve the matrix (co)polymer of choice. If the solvent that was used in the ion-exchange column and for the TAAOH neutralization also will dissolve the matrix (co)polymer, this step will not be

necessary. A preferred embodiment includes the 'switching' of solvent from that which the ion-exchange column was run to another which the TAA-neutralized polyelectrolyte and the matrix (co)polymer are both fully soluble. This process preferrably consists of adding the new solvent to the TAA-neutralized polyelectrolyte solution, then removing the original solvent with heating and application of vacuum (vacuum distillation). Other processes for affording this 'solvent switch' include precipitation of the TAA-neutralized polyelectrolyte with subsequent filtration of the polymer and redissolution in the new solvent. Once all of the original solvent has been removed, an appropriate amount of matrix (co)polymer, which has previously been dissolved in the same solvent, is added. As stated above, the amount of matrix polymer can be from 5 to 95 weight % and the amount of polyelectrolyte or hydrophilic copolymer can be from 95 to 5 weight % in the blend solution. Preferably, the matrix polymer is present in an amount ranging from 10 to 80%, more preferably 30 to 75 weight % and the polyelectrolyte is present between 20 to 90 weight % and more preferably 70 to 25 weight %in the blend solution. This blended solution is then cast into a thin film or further processed to yield a useful article such as an ion-exchange membrane.

Membrane formation

Casting of the blended solution can be carried out by many different procedures familiar to those skilled in the art. Particularly, solution casting with heating is selected. A quantity of the polymer blend solution is placed on an appropriate substrate. A sharp metal knife is then drawn across the substrate with a gap between the knife and the substrate. The thickness of this gap and the viscosity of the polymer blend solution control the thickness of the formed film. The thickness of the formed film is dependent on the end-use of the material, and can vary from 1.0 μm to 2.0mm. Preferrably, the formed film has a thickness of 10.0 μm to 500.0 μm and most preferrably from 20.0 μm to 250.0 μm. This 'wet' film is then dried in a air-circulating oven at elevated temperature. The time and temperature for drying the film can vary widely. The temperature used is from 20 °C to 250 °C, preferrably from 100 °C to 220 °C, and most preferrably from 120 °C to 200 °C. The drying time for the wet film can also vary widely. The oven residence time should be commercially

applicable and scalable in that it can be from 1.0 s to 24 h, preferrably from 1.0 min. to 2.0 h, and most preferrably from 1.0 min. to 45.0 min.

Small amounts of hydrophilic additives may be added to the polymer/block copolymer solution to help promote hydrophilicity. Useful additives include, but are not limited to polyethylene glycol (PEG), polyethylene glycol methacrylate (PEGMA),

The thickness of the final, dried film depends on the original thickness of the wet film before drying. This thickness will vary depending on the application intended for the final article. The thickness can be from 1.0 μm to 2.0 mm, preferrably from 5.0 μm to 500.0 μm, most preferrably from 10.0 μm to 300.0 μm. The dried film is removed from the substrate by typical methods familiar to those skilled in the art. Typically, the film is mechanically peeled from the substrate directly or with the aid of a metal knife. Alternatively, the film can be hydrated or submersed in water or solvent to aid in the removal of the film from the substrate.

In an as-cast polymer blend membrane, the polyelectrolyte component is associated with an organic counterion. An article, such as a membrane, produced from the polymer blend of the invention can be used as-is or the organic counterion may be exchanged with an acid or another counterion. The exchange can be conveniently done by washing the article in a solution containing the acid or salt with the appropriate counterion. The amount and type of counterion on the polyelectrolyte has a signficant impact on its ability to allow water permeation and reject salt. Preferred types of counterions for the polyelectrolyte include sodium, potassium, magnesium, and calcium. Especially preferred is sodium. The high water flux of the membrane of the invention makes it especially useful for water purification membranes, ion exchange resins, oil recovery, biological membranes, and the like.

In addition, cross-linking may be employed to improve dimensional stability. Cross-linking may be carried out by the action of an external agent on pendent functionalities present on the polyelectrolyte, the matrix (co)polymer, or combinations thereof. It is also feasible to incorporate internal cross-linking groups that are already pendent on either the polyelectrolyte or the matrix (co)polymer, which are then appropriately activated by application of an external impetus (heat or radiation).

The domain size of the polyelectrolyte in a cast film should be preferably less than 1.0 micron, and more preferably between 1 nm to 500 nm. The domain sizes

discussed herein are with respect to maximum domain sizes and/or average domain sizes. In a preferred embodiment, the domain sizes recited are the maximum domain sizes, but can be the average domain sizes. The polymer blend has a high degree of mechanical strength, a low swelling when hydrated, hydrolytic (chemical) stability, and a low level of sulfur loss (if sulfonated) in water, hot acid, oxidizing and/or reducing environments.

EXAMPLES

Example 1: Synthesis of vinylbenzyl alcohol (VBA)

A 12 L, three-necked round-bottom flask was equipped with mechanical stirrer, condensor, and thermocouple. To this flask was added 2.3 L of glacial acetic acid, 663.0 g of potassium acetate, and 613.7 g of vinylbenzyl chloride. This mixture was stirred at 110 °C for 18 h. Thin layer chromatography was the used to determine the extent of the reaction. The product was extracted with 2 L of ethyl acetate two times. The organic extracts were combined and washed with an aqueous solution of sodium bicarbonate until neutral (ph ~ 7) and then washed again with 2 L of water. Ethyl acetate was removed under reduced pressure to give 703 g of a light brown oil. (99% yield). ^{1}H NMR (DMSO-d6): δ 7.35 (m, 4H, aromatic), δ 6.70 (m, 1H, vinyl), δ 5.75 (d, 1H, vinyl), δ 5.25 (d, 1H, vinyl), δ 5.07 (s, 2H, benzyl), δ 2.07 (s, 3H, methyl ester).

A second 12 L flask equipped with mechanical stirrer, condensor, and thermocouple was charged with 761.0 g (13.56 mol) potassium hydroxide, 3.5 L (86.6 mol) of methanol, 1.1 L (58.38 mol) of water, and 703 g of vinylbenzyl acetate from the previous step producing a dark red-colored solution. The reaction was heated to reflux and followed by thin layer chromatography, which indicated that the reaction was complete after 1 h. The reaction mixture was cooled to room temperature and extracted twice with 4 L of diethyl ether. The ether layer was then washed with three times with 4 L of aqueous sodium chloride, then two times with 4 L of water. The ether layer was dried with $MgSO_4$ and filtered. Ether was removed from the filtrate under reduced pressure to give a brown oil. (487.0 g, 91% yield).

Example 2: Synthesis of vinylbenzyl sulfonate (VBS)

A 100 gal. glass-lined reactor was charged with 46.5 gal. of water and 20.0 gal. of acetone at room temperature. To that mixture was added 18.0 kg. of sodium sulfite, 1.0 kg. of sodium iodide, and 20.0 kg. of vinylbenzyl chloride (Dow Specialty Monomers, 55% meta 45% para isomer). This mixture was sparged with nitrogen for 30 min. then heated to 50 °C and maintained at that temperature for 24h. The acetone and approximately 20 gal. of water were then removed by vacuum distillation. The remaining slurry was cooled to 10 °C and filtered, recovering a light yellow solid. The filtrate was returned to the reactor, and an additional 15 gal. of water was removed by vacuum distillation. The solids were combined and dried in vacuo at 40 °C. Recovered yield was 13.1 kg (45% yield).

Example 3: Synthesis of Poly(sodium vinylbenzylsulfonate-*co*-vinylbenzyl alcohol) - Poly(NaVBS-*co*-VBA)

A 22-L round-bottom flask was charged with a slurry of NaVBS (3500 g, 15.893 mol) in house DI water (13.689 kg). Sparging with nitrogen was begun immediately. The mixture was heated to 50°C, at which point VBA (533 g, 3.973 mol) was added over a period of 10 min. The mixture was heated further to 80°C, followed by the introduction of the initiator. A solution of Vazo 56 WSP (3.110 g, 0.01147 mol, DuPont) in DI water (307.9 g) was added over a period of 10 min. Sparging was then halted, and the solution was kept under a blanket of nitrogen. The viscosity noticeably increased within 15 min, and a substantial exotherm became evident. A temperature excursion to over 90°C was controlled by sparging with nitrogen. After 2 h of reaction time, a second charge of Vazo 56 WSP (12.46 g, 0.04592 mol) in DI water (307.9 g) was added over a period of 10 min. The reaction was allowed to proceed for an additional 2 h (total reaction time was 4 h). Conversion was determined by ^{1}H NMR to be 85% at t = 2 h and 99% at t = 4 h. The composition of the copolymer was determined by ^{1}H NMR to be 22.2 ± 0.5 mol % benzyl alcohol units, which was in good agreement with the NaVBS-VBA feed ratio. The final concentration of polymer was estimated by gravimetry at 22.3 wt. %.

The sodium form polyelectrolyte was then ion-exchanged to the acid form using the following process. A glass column (30.5 cm in diameter, 122 cm in length) was equipped with a compressed nitrogen line (25 psi max. pressure) and deionized water inlet. DOWEX Marathon C ion-exchange resin (21.74 L, wet) was then added. This column was rinsed exhaustively with deionized water then charged with a 20 wt.

% solution of poly(sodium vinylbenzylsulfonate-co-vinylbenzyl alcohol) (3970 g) in deionized water (14.0 kg). The solution was forced through the column with nitrogen overpressure (up to 17 psig) at a rate of 0.4 bed volumes per hour and eluent was collected in fractions. The pH of the eluent was continuously tested with pH test strips in order to determine the presence of protonated polymer. Fractions containing the highest concentrations of polymer were combined to yield a 17.5 wt. % solution of poly(vinylbenzylsulfonic acid-co-vinylbenzyl alcohol) (2540 g, 69%) with 99.8% exchange efficiency (H^+ for Na^+) by elemental analysis and acid-base titration with NaOH to a phenolphthalein endpoint.

The acid-form polyelectrolyte was neutralized with tetrabutylammonium hydroxide using the following procedure. A 22-L round-bottom flask was then charged with 14.403 kg of a 17.5 wt. % solution of acid form Poly(VBSA-*co*-VBA) in DI water. The flask was kept on dry ice throughout the neutralization process. A 55.10 wt. % solution of TBAOH (4800 g, 10.18 mol TBAOH) was added to the stirred polymer solution over a period of several hours to produce a pH of 1.82 (approximately 95% of the acid groups neutralized). NMP (20.26 kg) was then added to the neutralized solution. The solution was heated to 80°C and purged vigorously with air. The water evaporated at a rate of approximately 0.5 L h^{-1}. The process was stopped when the water content was < 1000ppm, which was determined by Karl-Fisher titration. The final solution had a solids content of 20wt%.

Example 4: Blending of ammonium form poly(VBS-*co*-VBA) with KYNAR 2801.

6400g of the ammonium neutralized poly(VBS-*co*-VBA) in NMP from Example 3 was blended with 1225g of polyvinylidene fluoride (KYNAR 2801 from Arkema Inc.), and 4874g of NMP (ACS grade) using a high-shear mixer until the temperature of the solution reached 60°C. 171g of blocked isocyanate crosslinker (TRIXENE BL7982 from Baxenden Chemicals, Ltd.) and 9.9g of catalyst (FASCAT 4202 from Arkema) was incorporated into the solution after it had cooled to room temperature. The components were then mixed for several minutes on the high shear mixer.

The solution was then cast into 10 inch wide membrane using a slot die application method on a continuous coating process. The substrate was aluminum foil and the wet film was dried into a membrane in a 200° C oven for three minutes. The

thickness of the dried membrane was 1mil. Sheets of the membrane (roughly 10 inches by 8) were activated in acid to remove the ammonium salts.

For the activation, the membrane was immersed in 2200g of 1M aqueous hydrochloric acid (ACS grade acid and 18 MΩ deionized water). The acid bath was heated from ambient to 60-65°C over the span of approximately 75 min. The bath was then held in this temperature range for approximately 45 minutes. Subsequently, the membrane was washed in 18 MΩ deionized water and immersed in 2200g of 1M sulfuric acid (ACS grade acid and 18 MΩ deionized water). The acid bath was heated from ambient to 60-65°C over the span of approximately 75 min. The bath was then held in this temperature range for approximately 45 minutes. The membranes were removed from the sulfuric acid bath and washed with 18 MΩ deionized water to remove residual acid. The acid-form membrane was then dried at room temperature.

The ion exchange capacity (IEC) of the membrane was measured by the following procedure. Approximately 0.1g of dried membrane was immersed in 80mL of 21wt% sodium chloride solution. The solution and membrane were placed in 60°C water batch for 16 hours. The salt solution was titrated using a standardized potassium hydroxide solution with a phenolphthalein indicator. The data is reported in Table 1.

Example 5: Blending of ammonium form poly(VBS-*co*-VBA) with KYNAR 2801.

4008g of the ammonium neutralized poly(VBS-*co*-VBA) in NMP from Example 3 was blended with 942g of polyvinylidene fluoride (KYNAR 2801 from Arkema Inc.), and 4874g of NMP (ACS grade) using a high-shear mixer until the temperature of the solution reached 60°C. Two hours before the room temperature solution was cast into membrane, 92g of isocyanate crosslinker (DESMODUR N3300 from Bayer MaterialScience, LLC.) was added to the solution. The components were mixed using a mechanical stirrer for 5 minutes and the solution was rolled slowly on a jar mill until it was used.

The membrane was cast into a membrane and activated as described in Example 4.

Example 6: Formation of sodium form poly(VBS-*co*-VBA) with KYNAR 2801.

Two sheets of acid form membrane from Example 4 (size of each was approximately 7 inches by 7 inches) were immersed in 9000g of 21% sodium chloride solution that was preheated to 60°C. The solution and membrane were maintained at 60°C for 16 hours. The ion exchange was stopped by immersing the membrane in about 750mL of ambient temperature 18 MΩ deionized water for 30 minutes. Afterwards, each membrane was washed with deionized water exhaustively to remove residual sodium chloride from the membranes. Each membrane was washed at least eight times with deionized water (approximately 2 liters of water per wash).

Example 7:

An amphiphilic diblock copolymer was prepared by weighing 175g (0.40mol) of methoxy-terminated polyethyleneglycol methacrylate (MPEG(350)MA), 429g (5.0mol) of methyl acrylate (MA), and 25g (0.29mol) MAA in 50g butyl acetate. 19.14g (50.2mmol) BLOCBUILDER (Arkema Inc.) was added and the mixture heated to 105°C. The monomers were allowed to react for 3 hours at 105 °C to reach 61% conversion of MA and 95% conversion of both MAA and MPEGMA. The polymer and solvent mixture was stripped under vacuum at 60-70°C to remove most of the residual MA. To make the second block, added 359g MMA to a mixture of 70.0g first block, 3.9g MA, 16g butyl acetate, 121.76g acetone. The PMMA block was reacted at 105°C for 2 hours until reaching 55% conversion. Half of the resulting polymer was dried under vacuum at 130°C for 3 hours.

Example 8:

A neutralized block copolymer was prepared by dissolving 216g of the polymer from example 7 in 212g of additional acetone. To this solution was added 3.425g of 20% NaOH(aq). The resulting solution was dried under vacuum at 130°C for 3 hours

Example 9:

PVDF resin (15.0 g, avg Mw ~ 400,00 - 500,000) was mixed with 3.0 g of an acrylic co-polymer [PMMA (block Mw ~ 50,000) - block- PMA/MPEGMA/AA (block Mw ~ 3000, MPEGMA ~40%, PMA ~50%, AA ~10%)], N-methylpyrrolidone (NMP) solvent (82.0 g). This mixture was stirred at 65°C for 2 hours, until all

components were fully dissolved. The solution was allowed to set overnight to allow any air bubbles to dissipate. This solution was then used to cast membranes.

The solution was drawn down on an unprimed aluminum Q panel, using a wet film thickness of 30 um. The wet film was baked in an oven at 400°F for 10 minutes to obtain a dense film. The film was soaked in water for 15 minutes to permit release from the aluminum substrate. The dense film thickness was ~ 30 – 40 um. This film was used for water permeation testing.

Comparative Example 10:

PVDF resin (15. g, avg Mw ~ 4000,000 – 500,000) was dissolved by stirring in 85 g of N-methylpyrrolidone at 60°C for two hours. The solution was allowed to cool to room temperature and set overnight to degas.

The solution was drawn down on an unprimed aluminum Q panel, using a wet film thickness of 30 um. The wet film was baked in an oven at 400°F for 10 minutes to obtain a dense film. The film was soaked in water for 15 minutes to permit release from the aluminum substrate. The dense film thickness was ~30–40 um. This film was used for water permeation testing and represented an unmodified PVDF control sample.

Example 11: Performance characteristics of membranes

Water Permeability Test by Pressure Hold

47 mm disks were cut from PVDF film samples from Examples 4-6. NAFION 111 (a product E.I. DuPont de Nemours & Company distributed by Ion Power, Inc.) is a commercial material used as a comparison. These samples were placed in a pressure flow cell in a capillary flow porometer, and covered with 10 ml of water. The cell was sealed and the sample brought to 300 psi with compressed air. The cell was held at this pressure for 15 minutes. The cell was then opened and the remaining water measured and compared to the original volume. This "pressure hold" test provides a quick to compare water permeability through dense membranes. The table below shows water permeability measured by this test. No permeability was seen with the pure PVDF dense film, but found significant water permeation with both types of compolymer-PVDF blended films. These results confirm the enhanced water permeability of the PVDF-copolymer blends.

The rate of permeation of water through a membrane is a critical factor in judging its overall performance. Generally, higher permeation rates are desirable, thus

reducing the pressure required to force water through the membrane at an acceptable rate. The permeability of water through various membranes was determined using a dead-end cell. Table 1 shows water permeability versus membrane IEC. IEC is roughly a measure of the amount of acid groups present in the membrane and is generally proportional to the permeability of water. One can clearly see a general trend of increasing water permeability with increasing IEC. Also, the membrane in the sodium-form shows lower permeability, reinforcing the effect of changing the counterion has on membrane properties.

Table 1. Water permeability data for various membranes.

	Ion exchange Capacity (meq/g)	**Counterion**	**Pure Water Permeability (cm^2/s)**
Sample 4	1.14	H^+	$1.39x10^{-5}$
Sample 5	0.95	H^+	$5.04x10^{-6}$
Sample 6	--- (based on the sample 4)	Na^+	$5.44x10^{-6}$
NAFION 111	0.92	H^+	$1.48x10^{-5}$

1) NaCl Permeability

The ability of a water purification membrane to reject salt, while allowing pure water to permeate is of utmost importance, particularly for the desalination of sea water. Here, the permeation of sodium chloride (NaCl) for membranes of the invention and sulfonated polysulfones was measured. Generally, lower permeability (higher rejection) is desirable. NaCl permeation data was collected in a two-compartment permeation cell at approximately 25°C. The NaCl permeating from the donor to the receiver cell was monitoring by a conductivity probe inserted in the receiver cell. Data from the testing is shown in Table 2. The membranes with a lower IEC has a lower salt permeation. The sodium form of the membrane also shows lower NaCl permeation than the acid form membrane.

Table 2. NaCl permeability for various membrane samples at varying salt concentrations.

	Ion exchange Capacity (meq/g)	**Counterion**	**NaCl Permeability (cm^2/s) in 0.01 M NaCl**	**NaCl Permeability (cm^2/s) in 0.1 M NaCl**	**NaCl Permeability (cm^2/s) in 1 M NaCl**
Sample 4	1.14	H^+	8×10^{-9}	3×10^{-8}	1×10^{-7}
Sample 5	0.95	H^+	3×10^{-9}	1×10^{-8}	5×10^{-8}
Sample 6	1.14	Na^+	3×10^{-9}	2×10^{-8}	5×10^{-8}
NAFION 111	0.92	H^+	5×10^{-9}	3×10^{-8}	9×10^{-8}

What is claimed is:

1. A dense polymer membrane comprising:

a) 99-20 weight percent of a hydrophobic matrix polymer; and

b) 1-90 weight percent of a hydrophilic polymer,

wherein said hydrophobic matrix polymer and said hydrophilic polymer are compatible, and wherein said dense polymer membrane has a maximum pore size of 0.05 microns or less.

2. The polymer membrane of claim 1, wherein said hydrophilic polymer comprises a hydrophilicly active homopolymer or copolymer, or a polyelectrolyte.

3. The polymer membrane of claim 2, wherein said hydrophilic copolymer is a block copolymer.

4. The polymer membrane of claim 3, wherein said block copolymer is an amphiphilic block copolymer, having at least one hydrophilic block and at least one hydrophobic block.

5. The polymeric membrane of claim 2 wherein said block copolymer is a di-, tri- or multiblock copolymer.

6. The polymeric membrane of claim 5 wherein said tri-block copolymer consists of a hydrophilic middle block and hydrophobic end blocks.

7. The polymeric membrane of claim 5 wherein said tri-block copolymer consists of a hydrophobic middle block and hydrophilic end blocks.

8. The polymeric membrane of claim 4, wherein said amphiphilic block copolymer is formed by a controlled-radical polymerization process (CRP).

9. The polymeric membrane of claim 1 wherein said matrix comprises a fluoropolymer.

10. The polymeric membrane of claim 1 wherein said fluoropolymer is a polyvinylidene fluoride homopolymer, or a polyvinylidene copolymer comprising at least 50 mole percent of vinylidene fluoride monomer units.

11. The polymeric membrane of claim 1 having a maximum pore size of less than 0.02 um.

12. The polymeric membrane of claim 1 comprising 99 – 40 weight percent of hydrophobic matrix polymer and 1 – 60 weight percent of hydrophilic polymer.

13. The polymeric membrane of claim 12 comprising 90 – 70 weight percent of hydrophobic matrix polymer and 10 – 30 weight percent of hydrophilic polymer.

14. The polymeric membrane of claim 4, wherein said amphiphilic block copolymer is partially or fully neutralized.

15. The polymeric membrane of claim 4, wherein said hydrophilic and hydrophobic blocks comprise acrylic polymers.

16. The polymeric membrane of claim 1, wherein said hydrophobic matrix polymer and hydrophilic polymer form an intimate blend.

17. The polymeric membrane of claim 16, wherein said intimate blend is in the form of an interpenetrating polymer network (IPN) or a core-shell morphology.

18. The polymeric membrane of claim 2, wherein said polyelectrolyte contains sulfonate, phosphonate of carboxylate groups.

19. The polymeric membrane of claim 2, wherein said polyelectrolyte is selected from the group consisting of vinyl ether polyelectrolytes, styrenic polyelectrolytes, polyelectrolytes having backbone aromatic groups, sulfonated polyetherether ketone and sulfonated polyetherketoneketone.