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- (71) Applicant: SABIC GLOBAL TECHNOLOGIES B.V.
[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).
- (72) Inventor; and
(71) Applicant (for BZ only): BERZINIS, Albin Peter
[US/US]; 1 Noryl Avenue, Selkirk, New York 12158 (US).
- (72) Inventors: BAJAJ, Pooja; 1 Noryl Avenue, Selkirk, New York 12158 (US). HALBFINGER, Rachel Elizabeth; 1 Noryl Avenue, Selkirk, New York 12158 (US).
- (74) Agent: JAKIELA, Dennis J.; 20 Church Street, 22nd Floor, Hartford, Connecticut 06103 (US).

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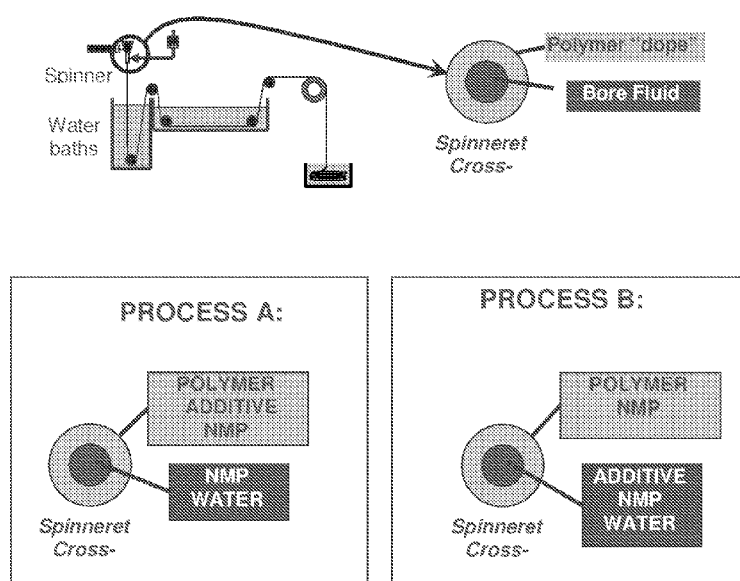
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[Continued on next page]

(54) Title: METHOD FOR MAKING POROUS ASYMMETRIC MEMBRANES AND ASSOCIATED MEMBRANES AND SEPARATION MODULES

Fig. 7



(57) Abstract: A method of making a porous asymmetric membrane involves dissolving a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, or a combination thereof in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition composed of water, a water-miscible polar aprotic solvent, or a mixture thereof, and a polymer additive dissolved in the first non-solvent composition. The method can be a method of making a hollow fiber by coextrusion through a spinneret having an annulus and a bore, including coextruding the membrane-forming composition through the annulus, and the first non-solvent composition through the bore, into a second non-solvent composition composed of water, a water-miscible polar aprotic solvent, or a mixture thereof to form the hollow fiber.



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METHOD FOR MAKING POROUS ASYMMETRIC MEMBRANES AND ASSOCIATED MEMBRANES AND SEPARATION MODULES

BACKGROUND OF THE INVENTION

[0001] Reverse osmosis is utilized in membrane separation process whereby a feed stock containing a solute, which has molecular or colloidal dimensions which are significantly greater than the molecular dimensions of its solvent, is depleted of the solute by being contacted with the membrane at such pressure that the solvent permeates the membrane and the solute is retained. This results in a permeate fraction which is solute-depleted and a retentate fraction which is solute-enriched. In ultrafiltration, nanofiltration and microfiltration, pressure in excess of the osmotic pressure can be used to force the solvent through the membrane. Drinking water production, the production of milk protein concentrate for cheese production, and enzyme recovery are examples of ultrafiltration processes based on reverse osmosis.

[0002] Poly(phenylene ether)s are a class of plastics having excellent water resistance, thermal resistance, and dimensional stability. They retain their mechanical strength in hot, and/or wet environments. Therefore they can be used for the fabrication of porous asymmetric membranes useful in various separation processes, including reverse osmosis. For example, poly(phenylene ether)s can be used in processes that require repeated cleaning with hot water or steam sterilization. Nonetheless, there remains a need for a porous asymmetric membrane having improved filtration properties, including materials that will improve selectivity without adversely affecting permeation flux.

[0003] Processes for making hollow fiber membranes rely on using relatively large amounts of polymer additives such as polyvinylpyrrolidone (PVP) in the dope solution, which contains the membrane-forming polymer, in order to obtain the desired pore size, pore distribution, and contact angle for the selective inner surface of the hollow fiber. The polymer additive must diffuse to the inner surface of the hollow fiber during coagulation of the membrane-forming polymer. Significant amounts of the polymer additive can remain trapped in the interior of the hollow fiber annular section and have little effect on pore formation on the inner selective layer. Also, the polymer additive can be incompatible with the membrane-forming polymer or insoluble in the dope solution.

[0004] A challenge is to develop a method for making porous asymmetric membranes in which the polymer additive does not cause incompatibility or solubility problems with the membrane-forming dope solution, and which efficiently delivers the polymer additive to the selective surface of the porous asymmetric membrane so the membrane properties for optimal membrane properties and performance.

BRIEF DESCRIPTION OF THE INVENTION

[0005] An improved method of making a porous asymmetric membrane comprises, consists essentially of, or consists of: dissolving a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, a polyethersulfone, a polysulfone, a polyphenylsulfone, a polyimide, a polyetherimide, polyvinylidene fluoride or a combination comprising at least one of the foregoing in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising a non-solvent comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, to form the porous asymmetric membrane.

[0006] In a specific embodiment, a method of making a porous asymmetric membrane comprises: dissolving a poly(phenylene ether) copolymer comprising 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol and 20 to 80 mole percent repeat units derived from 2-methyl-6-phenylphenol in N-Methyl-2-pyrrolidone to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising water, N-Methyl-2-pyrrolidone, and a polymer additive comprising poly(vinylpyrrolidone), poly(styrene-co-vinylpyrrolidone), polystyrene-block-poly(N,N-dimethylacrylamide) or a combination comprising at least one of the foregoing, dissolved in the first non-solvent composition, to form the porous asymmetric membrane.

[0007] A method of making a hollow fiber by coextrusion through a spinneret comprising an annulus and a bore, comprises coextruding: a membrane-forming composition comprising a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate), or a combination comprising at least one of the foregoing, through the annulus, and a first non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, through the bore, into a second non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, to form the hollow fiber. A hollow fiber made by the method can be fabricated into a separation module.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Referring now to the drawings, Fig. 1 depicts scanning electron microscopy (SEM) images of the porous asymmetric membrane surfaces Examples 6 and 9-10.

[0009] Fig. 2 depicts SEM images of the asymmetric membranes of Example 17 and Comparative Example 2.

[0010] Fig. 3 depicts a diagram of a laboratory scale, dry-wet immersion precipitation hollow fiber spinning apparatus.

[0011] Fig. 4 depicts laboratory-scale hollow fiber membrane modules.

[0012] Fig. 5 depicts a diagram of hollow fiber filtration system for measuring clean water flux and molecular weight cut-off.

[0013] Fig. 6 depicts SEM images of the hollow fiber membranes of Comparative Example 3 and Example 18.

[0014] Fig. 7 depicts diagrams of laboratory scale, dry-wet immersion precipitation hollow fiber spinning apparatus and spinneret cross-section indicating bore fluid in spinneret bore and polymer dope solution in spinneret annulus; the spinneret cross-section indicating NMP and water in bore fluid and membrane-forming polymer, polymer additive, and NMP in the dope solution (Process A); and the spinneret cross-section indicating NMP, water, and polymer additive in bore fluid and membrane-forming polymer and NMP in the dope solution (Process B).

[0015] Fig. 8 depicts SEM images of the asymmetric membranes of Example 21a (coagulation bath of 50/50 NMP-water), Example 22a (coagulation bath of 0.2 wt% PVP K30 in 50/50 NMP-water), and Example 23a (coagulation bath of 0.2 wt% PVP K90 in 50/50 NMP-water). The membrane-forming polymer is the 20/80 MPP-DMP copolymer of Example 11a.

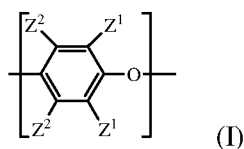
DETAILED DESCRIPTION OF THE INVENTION

[0016] An improved method of making porous asymmetric membranes includes adding a polymer additive to the coagulation solution, instead of the dope solution, which contains the membrane-forming polymer. The method is applicable to the production of hollow fibers as well as flat membranes. When the porous asymmetric membrane is as hollow fiber, the polymer additive is added to the bore fluid instead of the dope solution. Advantageously, the polymer additive is selectively incorporated at the inner surface of the hollow fiber. Issues arising from incompatibility of the polymer additive with the membrane-forming polymer or dope solution are eliminated. Advantageously, the method provides porous asymmetric membranes having surface pore size and pore density, water contact angle, clean water flux, and molecular weight cut-off values that make the porous asymmetric membranes suitable for fabrication into separation modules designed for purification of aqueous streams.

[0017] The improved method of making a porous asymmetric membrane comprises: dissolving a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether)

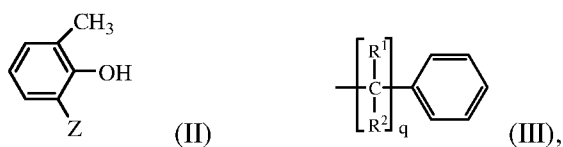
copolymer, a polyethersulfone, a polysulfone, a polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate) or a combination comprising at least one of the foregoing in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising a non-solvent comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the non-solvent, to form the porous asymmetric membrane. The hydrophobic polymer can be, for example, poly(2,6-dimethyl-1,4-phenylene ether), ULTRASON™ E, ULTRASON™ S, or ULTRASON™ P. A specific polyethersulfone is ULTRASON™ E 6020 P, available from BASF. A combination, or blend, of any of these hydrophobic polymers can also be used. In this way, the beneficial properties attributable to each individual polymer can be obtained in the blend.

[0018] In some embodiments, the hydrophobic polymer is a poly(phenylene ether) copolymer. The poly(phenylene ether) copolymer can comprise first and second repeat units independently having the structure (I):



wherein each occurrence of Z^1 is independently halogen, unsubstituted or substituted $\text{C}_1\text{-C}_{12}$ hydrocarbyl provided that the hydrocarbyl group is not tertiary hydrocarbyl, $\text{C}_1\text{-C}_{12}$ hydrocarbylthio, C_{1-12} hydrocarbyloxy, or C_{2-12} halohydrocarbyloxy, wherein at least two carbon atoms separate the halogen and oxygen atoms, wherein each occurrence of Z^2 is independently hydrogen, halogen, unsubstituted or substituted $\text{C}_1\text{-C}_{12}$ hydrocarbyl provided that the hydrocarbyl group is not tertiary hydrocarbyl, C_{1-12} hydrocarbylthio, C_{1-12} hydrocarbyloxy, or C_{2-12} halohydrocarbyloxy, wherein at least two carbon atoms separate the halogen and oxygen atoms, and wherein the first units and the second repeat units are different.

[0019] In some embodiments, the hydrophobic polymer comprises a poly(phenylene ether) comprising repeat units derived from 2,6-dimethylphenol. For example, the poly(phenylene ether) can comprise, consist essentially of, or consist of: 100 to 0 mole percent, specifically 90 to 20 mole percent, and more specifically 80 to 20 mole percent of repeat units derived from 2,6-dimethylphenol; and 0 to 100 mole percent, specifically 10 to 80 mole, and more specifically 20 to 80 mole percent of repeat units derived from a second monohydric phenol (II) wherein Z is C_{1-12} alkyl, C_{3-12} cycloalkyl, or monovalent group (III)



wherein q is 0 or 1, and R^1 and R^2 are independently hydrogen or C_{1-6} alkyl; wherein the poly(phenylene ether) copolymer has an intrinsic viscosity of 0.7 to 1.5 deciliters per gram, measured in chloroform at 25 °C. The first monohydric phenol can comprise 2-methyl-6-phenylphenol, and the hydrophobic polymer can comprise a copolymer having 20 mole percent of repeat units derived from 2-methyl-6-phenylphenol and 80 mole percent repeat units derived from 2,6-dimethylphenol. The copolymer can also be a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, or a terpolymer of 2,6-dimethylphenol and 2,6-trimethylphenol, and 2,3,6-trimethylphenol.

[0020] The hydrophobic polymer can be a poly(phenylene ether) copolymer having an intrinsic viscosity greater than or equal to 0.7, 0.8, 0.9, 1.0, or 1.1 deciliters per gram, and less than or equal to 1.5, 1.4, or 1.3 deciliters per gram, when measured in chloroform at 25 °C. In some embodiments, the intrinsic viscosity is 1.1 to 1.3 deciliters per gram.

[0021] In some embodiments, the poly(phenylene ether) copolymer has a weight average molecular weight of 100,000 to 500,000 daltons (Da), as measured by gel permeation chromatography against polystyrene standards. Within this range, the weight average molecular weight can be greater than or equal to 150,000 or 200,000 Da and less than or equal to 400,000, 350,000, or 300,000 Da. In some embodiments, the weight average molecular weight is 100,000 to 400,000 Da, specifically 200,000 to 300,000 Da. The poly(phenylene ether) copolymer can have a polydispersity (ratio of weight average molecular weight to number average molecular weight) of 3 to 12. Within this range, the polydispersity can be greater than or equal to 4 or 5 and less than or equal to 10, 9, or 8.

[0022] The solubility of the hydrophobic polymer in water-miscible polar aprotic solvents can be 50 to 400 grams per kilogram at 25 °C, based on the combined weight of the hydrophobic polymer and the solvent. Within this range, the solubility can be greater than or equal to 100, 120, 140, or 160 grams per kilogram, and less than or equal to 300, 250, 200, or 180 grams per kilogram at 25 °C. Advantageously, the use hydrophobic polymers having an intrinsic viscosity of 0.7 to 1.5 deciliters per gram, specifically 1.1 to 1.3 deciliters per gram, and a solubility of 50 to 400 grams per kilogram at 25 °C results in membrane-forming compositions with solution concentrations and viscosities that provides good control over the phase inversion step of membrane formation.

[0023] Additive polymers have been used to impart a suitable viscosity to membrane-forming compositions. They facilitate the formation of asymmetric porous membranes having

pore sizes, pore densities, and water contact angles suitable for purification of aqueous streams. However, polymer additives in the porous asymmetric membranes are prone to extraction in the coagulation (phase inversion) and washing steps of membrane fabrication. Moreover the polymer additive can be leached out of the membrane in the end-use application – membrane treatment of aqueous streams. For example, polyethersulfone can be blended with poly(N-vinylpyrrolidone), and the two polymers can be co-precipitated from solution to form a membrane. Excess poly(N-vinylpyrrolidone) must be washed off of the membrane with water, which results in a waste of valuable material, and which produces aqueous waste comprising the excess poly(N-vinylpyrrolidone) that is difficult to treat. Advantageously, when the polymer additive is introduced using the method disclosed herein, it is less prone to extraction during coagulation and in the end-use application.

[0024] The additive polymer can comprise hydrophilic functional groups, copolymerized hydrophilic monomers, or blocks of hydrophilic monomer repeat units. For example, the additive polymer can comprise a hydrophilic polymer or an amphiphilic polymer. An amphiphilic polymer is defined herein as a polymer that has both hydrophilic (water-loving, polar) and hydrophobic (water-hating, non-polar) properties. The amphiphilic polymer can be a random, alternating, periodic, graft, or block copolymer of hydrophilic and hydrophobic comonomers. The amphiphilic polymer can have star, comb, or brush branching. In some embodiments, the polymer additive comprises an amphiphilic block copolymer comprising a hydrophobic block and a hydrophilic block. For example, the amphiphilic block copolymer can comprise a hydrophobic block comprising polystyrene and a hydrophilic block or graft comprising poly(N,N-dimethylacrylamide) or poly(4-vinylpyridine). In some embodiments, the polymer additive comprises poly(vinyl pyrrolidone), poly(oxazoline), poly(ethylene glycol), poly(propylene glycol), a poly(ethylene glycol) monoether or monoester, a poly(propylene glycol) monoether or monoester, a block copolymer of poly(ethylene oxide) and poly(propylene oxide), polystyrene-graft-poly(ethylene glycol), polystyrene-graft-poly(propylene glycol), polysorbate, cellulose acetate, glycosaminoglycans such as heparin or heparin sulfate, or a combination comprising at least one of the foregoing.

[0025] The hydrophobic polymer is dissolved in a water-miscible polar aprotic solvent to form the membrane-forming composition. The water-miscible polar aprotic solvent can be, for example, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP), N-ethyl-2-pyrrolidone, dimethyl sulfoxide (DMSO), dimethyl sulfone, sulfolane, butyrolactone; and combinations comprising at least one of the foregoing. In some embodiments, the water-miscible polar aprotic solvent is N-methyl-2-pyrrolidone. The solubility of the hydrophobic polymer in the water-miscible polar aprotic solvent can be 50 to 400 grams

per kilogram at 25 °C, based on the combined weight of the poly(phenylene ether) and the solvent. Within this range, the solubility can be greater than or equal to 100, 120, 140, or 160 grams per kilogram, and less than or equal to 300, 250, 200, or 180 grams per kilogram at 25 °C. Advantageously, a hydrophobic solubility of 50 to 400 grams per kilogram provides membrane-forming compositions conducive to the formation of suitable porous membranes.

[0026] The first non-solvent composition comprises water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing. The water-miscible polar aprotic solvent can be any of the water-miscible polar aprotic solvents used for the membrane-forming composition. In some embodiments, the first non-solvent composition comprises 10 to 100 weight percent water and 0 to 90 weight percent N-methyl-2-pyrrolidone, based on the total weight of the first non-solvent composition. Within this range, the first non-solvent composition can comprise 20 to 80 weight percent, specifically 20 to 60 weight percent, water and 80 to 20 weight percent, specifically 80 to 40 weight percent, N-methyl-2-pyrrolidone. In some embodiments, the first non-solvent composition comprises about 30 weight percent water and about 70 weight percent N-methyl-2-pyrrolidone. The first non-solvent composition serves as a coagulation, or phase inversion, bath for the membrane-forming composition. The membrane is formed by contacting the membrane-forming composition with the first non-solvent composition. The copolymer, which is near its gel point in the membrane-forming composition, coagulates, or precipitates as a film or hollow fiber.

[0027] In some embodiments, the method further comprises washing the porous asymmetric membrane in a second non-solvent composition. This step serves to rinse any residual water-miscible polar aprotic solvent from the membrane. The first and second non-solvent compositions can be the same or different, and can comprise water, or a mixture of water and a water-miscible polar aprotic solvent. In some embodiments the first and second non-solvents are independently selected from water, and a water/N-methyl-2-pyrrolidone mixture. In some embodiments, the first and second non-solvents are both water. The water can be deionized. In some embodiments, the method further comprises drying the membrane to remove residual first and second non-solvent composition, for example water and N-methyl-2-pyrrolidone.

[0028] The method includes phase-inverting the membrane-forming composition in the first non-solvent composition. Any of several techniques for phase inversion can be used. For example, the phase inversion can be a dry-phase separation method in which the dissolved copolymer is precipitated by evaporation of a sufficient amount of solvent mixture to form the membrane. The phase inversion step can also be a wet-phase separation method in which the dissolved copolymer is precipitated by immersion in the first non-solvent to form the membrane.

The phase inversion step can be a dry-wet phase separation method, which is a combination of the dry-phase and the wet-phase methods. The phase inversion step can be a thermally-induced separation method in which the dissolved copolymer is precipitated or coagulated by controlled cooling to form the membrane. The membrane, once formed, can be subjected to membrane conditioning or pretreatment, prior to its end-use. The conditioning or pretreatment can be thermal annealing to relieve stresses or pre-equilibration in the expected feed stream.

[0029] In some embodiments, the method of making a porous asymmetric membrane comprises: dissolving a poly(phenylene ether) copolymer comprising 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol; and 20 to 80 mole percent repeat units derived from 2-methyl-6-phenylphenol in N-Methyl-2-pyrrolidone to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising water, N-Methyl-2-pyrrolidone, and a polymer additive comprising poly(vinylpyrrolidone), poly(styrene-co-vinylpyrrolidone), polystyrene-block-poly(N,N-dimethylacrylamide) or a combination comprising at least one of the foregoing, dissolved in the first non-solvent composition, to form the porous asymmetric membrane.

[0030] A porous asymmetric membrane is made by the method comprising: dissolving a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, a polyethersulfone, a polysulfone, a polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate) or a combination comprising at least one of the foregoing in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising a non-solvent comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the non-solvent, to form a porous asymmetric membrane having a substantially non-porous surface layer. The description of the method herein is also applicable to the porous asymmetric membrane made by the method. For example, the porous asymmetric membrane can comprise a poly(phenylene ether) copolymer comprising 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol; and 20 to 80 mole percent repeat units derived from 2-methyl-6-phenylphenol; and a polymer additive comprising poly(vinylpyrrolidone), poly(styrene-co-vinylpyrrolidone), polystyrene-block-poly(N,N-dimethylacrylamide), or a combination thereof.

[0031] The porous asymmetric membrane made by the method exhibits many advantageous surface properties. The polymer additive is incorporated into the selective surface layer of the porous asymmetric membrane by the method, which advantageously reduces the water contact angle of the surface compared to a porous asymmetric membrane made from the hydrophobic polymer without the polymer additive. For example, the porous asymmetric

membrane can have a water contact angle of greater than or equal to 20, 30, or 40 degrees, and less than or equal to 80, 70, or 60 degrees. In some embodiments, the porous asymmetric membrane has a water contact angle of 40 to 80 degrees. The porous asymmetric membrane made by the method can have a mean surface pore size distribution on the selective layer of greater than or equal to 1, 5, 10 nanometers (nm) and less than or equal to 100, 50, or 20 nm $\pm$ 1, 2, 5, or 10 nm. The porous asymmetric membrane made by the method can also have a surface pore density of greater than or equal to 100, 200, or 400 pores per μm^2 and less than or equal to 4,000, 2,400, or 1,200 pores per μm^2 .

[0032] The method is also applicable to making hollow fibers by coextrusion of a dope solution and a bore fluid, in which the membrane-forming composition is the dope solution and the first non-solvent composition is the bore fluid. Thus in some embodiments, a method of making a hollow fiber by coextrusion through a spinneret comprising an annulus and a bore, comprises coextruding: a membrane-forming composition comprising a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate), or a combination comprising at least one of the foregoing, through the annulus, and a first non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, through the bore, into a second non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, to form the hollow fiber.

[0033] In some embodiments the method further comprises washing the hollow fiber in a third non-solvent composition. This step serves to rinse any residual water-miscible polar aprotic solvent from the hollow fibers. The second and third non-solvent compositions can be the same or different, and can comprise water, or a mixture of water and a water-miscible polar aprotic solvent. In some embodiments the first and second non-solvent compositions are independently selected from water, and a mixture of water and N-Methyl-2-pyrrolidone. In some embodiments, the second and third non-solvent compositions are each water. The water can be deionized. In some embodiments, the method further comprises drying the hollow fiber to remove residual first and second non-solvent composition, for example water and N-methyl-2-pyrrolidone.

[0034] A hollow fiber is made by coextruding through a spinneret comprising an annulus and a bore: a membrane-forming composition comprising a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl

methacrylate), or a combination comprising at least one of the foregoing, through the annulus, and a first non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, through the bore, into a second non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, to form the hollow fiber.

[0035] The hollow fibers can be used in various separation modules. Thus in some embodiments, a separation module comprises hollow fiber made by coextruding through a spinneret comprising an annulus and a bore: a membrane-forming composition comprising a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate), or a combination comprising at least one of the foregoing, through the annulus, and a first non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, through the bore, into a second non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, to form the hollow fiber.

[0036] The configuration of the porous asymmetric membrane made by the method can be sheet, disc, spiral wound, plate and frame, hollow fiber, capillary, or tubular. Outside-in and inside-out separations are applicable to hollow fiber membranes, capillary membranes, and tubular membranes, each having an inner and outer surface in contact with the feed and retentate or the permeate.

[0037] The porous asymmetric membrane made by the method can be a porous hollow fiber. The wall thickness of the hollow fiber can be 20 to 100 micrometers (μm). Within this range, the wall thickness can be greater than 30 and less than or equal to 80, 60, 40, or 35 μm . In another embodiment the diameter can be 50 to 3000 μm , specifically 100 to 2000 μm . The membrane can comprise a substantially non-porous surface layer, and the non-porous surface layer can be on the inside surface of the hollow fiber. A separation module can comprise bundles of porous hollow fibers. In some embodiments, the fiber bundle comprises 10 to 10,000 porous hollow fibers. The hollow fibers can be bundled longitudinally, potted in a curable resin on both ends, and encased in a pressure vessel to form the hollow fiber module. Hollow fiber modules can be mounted vertically or horizontally.

[0038] The porous asymmetric membrane made by the method can be used for treatment of various aqueous, non-aqueous (e.g., hydrocarbon), or gaseous streams. Thus in some embodiments, a separation module comprises the porous asymmetric membrane made by a

method comprising: dissolving a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, a polyethersulfone, a polysulfone, a polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate), or a combination comprising at least one of the foregoing in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising a non-solvent comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the non-solvent, to form a porous asymmetric membrane having a substantially non-porous surface layer. The separation module can be designed for dead-end separation, cross-flow separation, inside-out separation, or outside-in separation.

[0039] Depending upon porous asymmetric membrane surface pore size distribution and pore density, and the end-use, the separation module fabricated from the porous asymmetric membrane made by the method can be a media filtration module, a microfiltration module, an ultrafiltration module, a nanofiltration module, or a reverse osmosis module. The separation module fabricated from the porous asymmetric membrane made by the method can also be a membrane contactors module, a pervaporation module, a dialysis module, an osmosis module, an electrodialysis module, a membrane electrolysis module, an electrophoresis module, or a membrane distillation module. For media filtration, the surface pore size can be about 100 to about 1,000 micrometers (μm). For microfiltration, the surface pore size can be about 0.03 to about 10 μm . For ultrafiltration, the surface pore size can be about 0.002 to 0.1 μm . For nanofiltration, the surface pore size can be about 0.001 to about 0.002 μm . For reverse osmosis, the surface pore size can be about 0.0001 to 0.001 μm . The porous asymmetric membranes described herein are surprisingly well suited for ultrafiltration and nanofiltration. In some embodiments, the porous asymmetric membrane has a surface pore size of 0.001 to 0.05 μm , specifically 0.005 to 0.01 μm .

[0040] The molecular weight cut off (MWCO) of a membrane is the lowest molecular weight solute in which 90 weight percent (wt%) or greater of the solute is retained by the membrane. The porous asymmetric membranes made by the method can have a MWCO of 500 to 40,000 daltons (Da), specifically 1,000 to 10,000 Da, more specifically 2,000 to 8,000 Da, or still more specifically 3,000 to 7,000 Da. Furthermore, any of the foregoing MWCO ranges can be present in combination with a desirable permeate flux, such as clean water permeate flux (CWF). For example, the permeate flux can be 1 to 200, specifically 2 to 100, more specifically 4 to 50 $\text{L}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$, wherein L is liters and m^2 is square meters. The porous asymmetric membranes made by the method can also provide a CWF of about 10 to about 80 $\text{L}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$, about 20 to about 80 $\text{L}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$, or about 40 to about 60 $\text{L}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$.

[0041] Flux across the membrane is driven by the osmotic or absolute pressure differential across the membrane, referred to herein as the trans-membrane pressure (TMP). The trans-membrane pressure can be 1 to 500 kilopascals (kPa), specifically 2 to 400 kPa, and more specifically 4 to 300 kPa.

[0042] The porous asymmetric membranes made by the method are useful for treatment of a variety of aqueous streams. Depending upon surface pore size distribution and pore density, and the configuration of the porous asymmetric membrane, the porous asymmetric membrane can be used to remove one or more of the following contaminants from water: suspended matter, particulate matter, sands, silt, clays, cysts, algae, microorganisms, bacteria, viruses, colloidal matter, synthetic and naturally occurring macromolecules, dissolved organic compounds, and salts. Thus, separation modules fabricated from the porous asymmetric membranes made by the method can be used in wastewater treatment, water purification, food processing, and in the dairy, biotechnology, pharmaceutical, and healthcare industries.

[0043] The porous asymmetric membranes made by the method, and separation modules fabricated from the porous asymmetric membranes made by the method, can advantageously be used in medical, pharmaceutical, biotechnological, or food processes, for example the removal of salts and/or low molecular weight organic impurities from aqueous streams by ultrafiltration, which results in increased concentration of a material having a molecular weight above the cut-off of the porous asymmetric membrane in an aqueous stream. The aqueous stream can be human blood, animal blood, lymph fluids, microbial or cellular suspensions, for example suspensions of bacteria, alga, plant cells, or viruses. Specific medical applications include the concentration and purification of peptides in blood plasma; hemofiltration; hemodialysis; hemodiafiltration; and renal dialysis. Other applications include enzyme recovery and desalting of proteins. Specific food applications include ultrafiltration of meat products and by-products, plant extracts, suspensions of algae or fungi, vegetable food and beverages containing particles such as pulp, and the production of milk protein concentrate for the production of cheese. Other applications include downstream processing of fermentation broths; concentration of protein in whole egg or egg white with simultaneous removal of salts and sugars; and concentration of gelling agents and thickeners, for example agar, carrageenan, pectin, or gelatin. Since a separation module fabricated from the porous asymmetric membrane made by the process is useful for a wide variety of aqueous fluid separation applications in many different fields, it may be applicable to other fluid separation problems not expressly disclosed herein as well.

[0044] Separation modules fabricated from the porous asymmetric membrane made by the method can be designed for liver dialysis or hemodialysis, for oxygenation of blood, such as in an artificial lung device, for separation of polysaccharides, for protein or enzyme recovery, for

membrane distillation, for wastewater treatment, for the production of purified water, e.g., drinking water, and for pretreatment of water in desalination systems. The separation module can be used to remove contaminants, including biological contaminants such as bacteria or protozoa, or organic chemical contaminants such as polychlorinated biphenyls (PCBs), to produce purified product streams.

[0045] The invention includes at least the following embodiments.

[0046] Embodiment 1. A method of making a porous asymmetric membrane, wherein the method comprises, consists essentially of, or consists of: dissolving a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, a polyethersulfone, a polysulfone, a polyphenylsulfone, a polyimide, a polyetherimide, polyvinylidene fluoride or a combination comprising at least one of the foregoing in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising a non-solvent comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, to form the porous asymmetric membrane.

[0047] Embodiment 2. The method of embodiment 1, further comprising washing the porous asymmetric membrane in a second non-solvent composition.

[0048] Embodiment 3. The method of embodiment 1 or 2, further comprising drying the porous asymmetric membrane.

[0049] Embodiment 4. The method of any of embodiments 1-3, wherein the hydrophobic polymer comprises a poly(phenylene ether) copolymer comprising first and second repeat units independently having the structure (I), wherein each occurrence of Z^1 is independently halogen, unsubstituted or substituted C_{1-12} hydrocarbyl provided that the hydrocarbyl group is not tertiary hydrocarbyl, C_{1-12} hydrocarbylthio, C_{1-12} hydrocarbyloxy, or C_{2-12} haloalkoxy, wherein at least two carbon atoms separate the halogen and oxygen atoms; wherein each occurrence of Z^2 is independently hydrogen, halogen, unsubstituted or substituted C_{1-12} hydrocarbyl provided that the hydrocarbyl group is not tertiary hydrocarbyl, C_{1-12} hydrocarbylthio, C_{1-12} hydrocarbyloxy, or C_{2-12} haloalkoxy, wherein at least two carbon atoms separate the halogen and oxygen atoms; and wherein the first units and the second repeat units are different.

[0050] Embodiment 5. The method of any of embodiments 1-4, wherein the hydrophobic polymer comprises a poly(phenylene ether) copolymer comprising, consisting essentially of, or consisting of 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol; and 20 to 80 mole percent repeat units derived from derived from a second

monohydric phenol (II), wherein Z is C₁₋₁₂ alkyl or cycloalkyl, or a monovalent group (III), wherein q is 0 or 1, and R¹ and R² are independently hydrogen or C₁₋₆ alkyl; wherein the poly(phenylene ether) copolymer has an intrinsic viscosity of 0.7 to 1.5 deciliters per gram, measured in chloroform at 25 °C.

[0051] Embodiment 6. The method of any of embodiments 1-5, wherein the polymer additive comprises poly(vinyl pyrrolidone), poly(oxazoline), poly(ethylene glycol), poly(propylene glycol), a poly(ethylene glycol) monoether or monoester, a poly(propylene glycol) monoether or monoester, a block copolymer of poly(ethylene oxide) and poly(propylene oxide), polystyrene-graft-poly(ethylene glycol), polystyrene-graft-poly(propylene glycol), polysorbate, cellulose acetate, glycosaminoglycans such as heparin or heparin sulfate, or a combination comprising at least one of the foregoing.

[0052] Embodiment 7. The method of any of embodiments 1-6, wherein the polymer additive comprises an amphiphilic block copolymer comprising a hydrophobic block and a hydrophilic block.

[0053] Embodiment 8. The method of any of embodiments 1-7, wherein the polymer additive comprises polystyrene-block-poly(N,N-dimethylacrylamide), polystyrene-block-poly(4-vinylpyridine), or a combination thereof.

[0054] Embodiment 9. The method of any of embodiments 1-8, wherein the first non-solvent composition comprises 10 to 100 weight percent water and 0 to 90 weight percent N-methylpyrrolidone, based on the total weight of the first non-solvent composition.

[0055] Embodiment 10. The method of embodiment 1, wherein the hydrophobic polymer comprises a poly(phenylene ether) copolymer comprising 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol; and 20 to 80 mole percent repeat units derived from 2-methyl-6-phenylphenol; the water-miscible polar aprotic solvent is N-methyl-2-pyrrolidone; and the polymer additive comprises poly(vinylpyrrolidone), poly(styrene-co-vinylpyrrolidone), polystyrene-block-poly(N,N-dimethylacrylamide), or a combination comprising at least one of the foregoing.

[0056] Embodiment 10a. A method of making a porous asymmetric membrane, wherein the method comprises, consists essentially of, or consists of: dissolving a poly(phenylene ether) copolymer comprising 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol and 20 to 80 mole percent repeat units derived from 2-methyl-6-phenylphenol in N-methyl-2-pyrrolidone to provide a membrane-forming composition; and phase-inverting the membrane-forming composition in a first non-solvent composition comprising water, N-methyl-2-pyrrolidone, and a polymer additive comprising poly(vinylpyrrolidone), poly(styrene-co-vinylpyrrolidone), polystyrene-block-poly(N,N-dimethylacrylamide), or a combination

comprising at least one of the foregoing, dissolved in the first non-solvent composition, to form the porous asymmetric membrane.

[0057] Embodiment 11. A porous asymmetric membrane made by the method of any of embodiments 1-10.

[0058] Embodiment 12. The porous asymmetric membrane of embodiment 11, having a water contact angle of 40 to 80 degrees.

[0059] Embodiment 13. A separation module comprising the porous asymmetric membrane of embodiment 11 or 12.

[0060] Embodiment 14. A method of making a hollow fiber by coextrusion through a spinneret comprising an annulus and a bore, wherein the method comprises, consists essentially of, or consists of: coextruding: a membrane-forming composition comprising a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate), or a combination comprising at least one of the foregoing, through the annulus, and a first non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, through the bore, into a second non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, to form the hollow fiber.

[0061] Embodiment 15. The method of embodiment 14, further comprising washing the hollow fiber in a third non-solvent composition.

[0062] Embodiment 16. The method of embodiment 14 or 15, further comprising drying the hollow fiber.

[0063] Embodiment 17. A hollow fiber made by the method of any of embodiments 14-16.

[0064] Embodiment 18. The hollow fiber of embodiment 17, wherein the hollow fiber has a substantially non-porous surface layer.

[0065] Embodiment 19. A separation module comprising the hollow fiber of embodiment 17 or 18.

[0066] Embodiment 20. The method of embodiment 5, wherein the first monohydric phenol is 2-methyl-6-phenylphenol.

[0067] Embodiment 21. The method of any one of embodiments 1-10 and 20, wherein the hydrophobic polymer has an intrinsic viscosity of 0.7 to 1.5 deciliters per gram, measured in chloroform at 25 °C.

[0068] Embodiment 22. The method of any of embodiments 1-10 and 20-21, wherein the solubility of the hydrophobic polymer in the water-miscible polar aprotic solvent is 50 to 400 grams per kilogram at 25 °C, based on the combined weight of the poly(phenylene ether) copolymer and the solvent.

[0069] Embodiment 23. The method of embodiment 7, wherein the amphiphilic block copolymer comprises 20 to 50 weight percent of the hydrophobic block and 50 to 80 weight percent of the hydrophilic block or graft.

[0070] Embodiment 24. The method of embodiment 7, wherein the hydrophilic block comprises poly(ethylene oxide) or a copolymer of ethylene oxide with 1,2-propylene oxide, 1,2-butylene oxide, styrene oxide, or a combination comprising at least one of the foregoing.

[0071] Embodiment 25. The method of embodiment 7, wherein the hydrophilic block or graft comprises an addition polymer of methoxy-capped poly(ethylene oxide) methacrylate, 4-vinylpyridine, N-vinylpyrrolidone, N,N-dimethylacrylamide, 4-acryloylmorpholine, or a combination comprising at least one of the foregoing.

[0072] Embodiment 26. The method of embodiment 4 or 5, wherein the hydrophobic polymer further comprises poly(2,6-dimethyl-1,4-phenylene ether), polyethersulfone, polysulfone, polyphenylsulfone, or a combination comprising at least one of the foregoing.

[0073] Embodiment 27. A porous asymmetric membrane made by the method of any of embodiments 20-26.

[0074] Embodiment 28. The porous asymmetric membrane of embodiment 27, having a water contact angle of 40 to 80 degrees.

[0075] Embodiment 29. The porous asymmetric membrane of any of embodiments 11-12 and 27-28, wherein a configuration of the porous asymmetric membrane is a sheet, disc, spiral wound, plate and frame, hollow fiber, capillary, and tubular.

[0076] Embodiment 30. The porous asymmetric membrane of any of embodiments 11-12 and 27-29, wherein the membrane is a porous asymmetric flat sheet.

[0077] Embodiment 31. The porous asymmetric membrane of any of embodiments 11-12 and 27-30, wherein the asymmetric membrane is in a form of a spiral.

[0078] Embodiment 32. The porous asymmetric membrane of any of embodiments 11-12 and 27-31, wherein the membrane is a porous asymmetric hollow fiber.

[0079] Embodiment 33. A separation module comprising the porous asymmetric membrane of any of embodiments 11-12 and 27-32.

[0080] The invention is further illustrated by the following non-limiting examples.

PREPARATIVE EXAMPLES: SYNTHESIS OF MPP-DMP COPOLYMERS

[0081] The copolymerizations were conducted in a bubbling polymerization reactor equipped with a stirrer, temperature control system, nitrogen padding, oxygen bubbling tube, and computerized control system. There were also feeding pot and pump for dosing reactants into the reactor.

Table 1. Materials

Abbreviation	Chemical Name
DMP	2,6-Dimethylphenol
MPP	2-Methyl-6-phenylphenol
DBA	Di- <i>n</i> -butylamine
DBEDA	N,N'-Di- <i>tert</i> -butylethylenediamine
DMBA	N,N-Dimethylbutylamine
QUAT	Didecyltrimethyl ammonium chloride
NTA	Nitrilotriacetic acid
CAT	Solution of Cu ₂ O in concentrated HBr, 6.5 wt.% Cu
NMP	N-Methyl-2-pyrrolidone, available from ThermoFisher.
6020P	A polyethersulfone (PES), available from BASF as ULTRASON™ E 6020 P.
PES	A polyethersulfone, available from BASF as ULTRASON™ E 6020 P.
PVP K30	Poly(vinyl pyrrolidone) having a K value of 26-35, calculated for a 1% aq. solution by the Finkentscher equation; and available from Aldrich.
PVP K90	Poly(vinyl pyrrolidone) having a K value of 90-100, calculated for a 1% aq. solution by the Finkentscher equation; and available from Aldrich.

PREPARATIVE EXAMPLE 1: PREPARATION OF MPP-DMP COPOLYMER WITH 50 MOLE PERCENT MPP IN 1.8-LITER REACTOR

[0082] Toluene (622.88 grams), DBA (8.1097 grams), DMBA (30.71 grams), and 5.44 grams of a diamine mix consisting of 30 weight percent (wt.%) DBEDA, 7.5 weight percent QUAT, and the balance toluene, were charged to a bubbling polymerization reactor and stirred under a nitrogen atmosphere at 25°C. A mix of 6.27 grams HBr and 0.5215 grams Cu₂O was added. Oxygen flow to the vessel was begun after 4 minutes of monomer mixture addition. The reactor temperature was ramped to 40° C in 18 min, maintained at 40 °C for 57 min, ramped to 45 C in 11 min, maintained at 45 °C for 33 min and ramped to 60 °C in 10 min. 403.67 grams of monomer solution (20.3 wt.% DMP, 30.6 wt.% MPP and 49. 1 wt. % toluene) was added over 35 minutes. Oxygen flow was maintained for 115 minutes, at which point the oxygen flow was stopped and the reaction mixture was immediately transferred to a vessel containing 11.07 grams NTA salt and 17.65 grams DI (deionized) water. The resulting mixture was stirred at 60 °C for 2 hours, and the layers were then allowed to separate. The decanted light phase was precipitated in methanol, filtered, reslurried in methanol, and filtered again. The copolymer was obtained as a dry powder after drying in a vacuum oven under nitrogen blanket at 110 °C.

PREPARATIVE EXAMPLES 2-4:

PREPARATION OF MPP-DMP COPOLYMERS WITH 20, 50, AND 80 MOLE % MPP WITH INTRINSIC VISCOSITIES OF ~ 1 DECILITER PER GRAM

[0083] The process of Preparative Example 1 was scaled to a one gallon steel bubbling reactor and copolymerization was conducted in similar fashion as described above. The ingredients for the batch reactor charges and continuous monomer feed solution are shown in Table 2. After charging the reactor the contents were brought with stirring to 25 °C before starting the continuous feed of monomer in toluene and then oxygen feed. The monomer/toluene mixture was fed over 45 minutes, and oxygen feed was maintained until 130 minutes. The reactor temperature was ramped to 45 °C at 90 minutes and then ramped to 60 °C at 130 minutes. The reaction contents were then transferred to a separate vessel for addition of NTA to chelate the copper, followed by separation of the toluene solution from the aqueous phase in centrifuge, precipitation of the copolymer solution into methanol as described above.

Table 2. Material Amounts for Preparative Examples 2-4

	Example 2	Example 3	Example 4
Reactor Charge (g)	20/80	50/50	80/20
cAT	17.3	21.6	17.3
DBEDA	5.3	6.7	5.3
DBA	9.9	9.9	9.9
DMBA	34.3	33.3	32.5
QUAT	1.6	2.0	1.6
DMP/TOLUENE 50/50	29.5	18.5	5.5
TOLUENE	2961.0	2961.0	2961.0
MPP	5.6	14.0	16.0
Continuous Feed Solution			
DMP/TOLUENE 50/50	364.5	228	64
MPP	69.4	172	197
Total	3498.36	3466.925	3310.08

The dried copolymers were characterized for molecular weight distribution via gel permeation chromatography (GPC) using CHCl₃ as solvent and referenced to polystyrene standards. The intrinsic viscosity (IV) of the resins was measured in CHCl₃ solution using an Ubbelohde viscometer and expressed in units of deciliters per gram (dL/g). The glass transition temperature T_g was measured using differential scanning calorimetry (DSC) and expressed in °C. The results for examples 1-4 are summarized in Table 3.

Table 3. Characterization of MPP-DMP Copolymers of Preparative Examples 1-4

Ex. No.	Scale	MPP/DMP (mole/mole)	GPC Mn (g/mole)	GPC Mw (g/mole)	GPC D (Mw/Mn)	IV in CHCl ₃ (dL/g)	T _g °C
1	1.8 liter	50/50	20,213	219,130	10.8	0.83	185
2	1 gallon	20/80	50,310	172,100	3.4	1.04	210
3	1 gallon	50/50	39,820	194,900	4.9	0.97	187
4	1 gallon	80/20	22,620	241,000	10.7	0.96	177

EXAMPLE 5 AND COMPARATIVE EXAMPLE 1: MEMBRANE CAST FROM 50/50 MPP/DMP COPOLYMER VS. COMPARATIVE EXAMPLE CAST FROM PES/PVP

[0084] A sample of polyethersulfone (PES) having a high molecular weight, and of a grade typically used to cast hollow fiber membranes for hemodialysis was dissolved in NMP at 16 wt.% in combination with 8 wt.% of polyvinylpyrrolidone (PVP) K-30 resin. In Comparative Example 1, this solution was cast into a membrane in the laboratory following the procedure described above. In Example 5, a solution of the MPP/DMP copolymer of Preparative Example 1 at 16 wt.% in NMP was prepared and cast into a membrane following the same process to prepare Example 5. The results of SEM image analysis of these two membranes are presented in Fig. 2, and a summary of characterization data for these membranes is provided in Table 4.

Table 4. Membrane Properties of Example 5 vs. Comparative Example 1

Ex.	NMP Casting Dope		Membrane				
	(Polymer, wt%)	Viscosity (cp at 20°C)	Surface Pore size distribution (nm)	Mean Cross-sectional thickness (μm)	Extent of Macrovoid Formation	Water flow, (g/hr-atm)	Contact Angle, Water
CE1	16% PES +8% PVP	3,065	7.3 ± 1.9	128	high	25	70
E5	16% Ex. 1	3,533	9.3 ± 3.2	40	low	39	82

The surface appearance of the membrane of Example 5 compares very well to the Comparative Example 1, and the digital image analysis confirms that Example 5 achieves a very similar pore size distribution in the absence of a pore-forming agent such as PVP. The cross-sectional morphology of Example 5 shows the formation of the desired co-continuous or “sponge” morphology to a large extent even in the absence of the PVP additive. The solution viscosity of Example 5 of our invention also compares well to that of the Comparative Example 1 which relies on addition of PVP to create a casting dope of suitable viscosity.

[0085] The water flow data indicates that the pores visible at the surface of Example 5 via SEM do indeed connect throughout the sample to allow the passage of water in a manner at least equivalent to that of Comparative Example 1, which is rather remarkable in the absence of the PVP additive. These results demonstrate that MPP-DMP copolymers of sufficiently high IV are capable of forming well-structured membranes via phase-inversion casting with solvents such as NMP without requiring the use of fugitive pore-forming additives such as PVP. Comparative Example 1 shows only a modest reduction in contact angle compared to Example 5, despite using a high concentration of the hydrophilic PVP additive in the casting dope.

EXAMPLES 5-10: GENERAL PROCEDURE FOR CASTING MEMBRANES VIA SOLVENT/NON-SOLVENT PHASE INVERSION PROCESS

[0086] In general, porous, asymmetric membranes were cast by dissolving MPP-DMP copolymers in NMP at concentrations of around 16 wt.%; pouring the viscous casting solution

onto a glass plate and drawing a thin film 150-250 micrometers thick across the plate by means of a casting knife. The glass plate bearing the thin film of MPP-DMP in NMP was placed into a primary coagulation bath over a time period of 10-15 minutes. The primary coagulation bath was a mixture of NMP and water, and promoted the precipitation and coagulation of the copolymer into an asymmetric porous membrane. The coagulated copolymer film floated free of the glass plate when coagulation was substantially complete, at which time it was transferred to a second bath in which it was soaked and rinsed in clean water to remove residual NMP.

[0087] The process is described in more detail as follows. The test copolymer was dissolved in N-methyl-2-pyrrolidone (NMP), chromatography grade, totaling 8-10 grams in a 20 milliliter (mL) glass vial, sealed tightly, and placed on a low speed roller for 13-48 hours until it forms a homogenous solution. The solution was poured in an oblong puddle and an adjustable height doctor blade was used to drag across the glass plate at a constant speed by hand. The entire glass plate bearing the cast copolymer solution was fully submerged into an initial non-solvent bath (25-100 wt.% DI water in NMP) until the membrane begins to lift off the plate. The membrane was transferred off of the glass plate into the intermediate non-solvent bath of 100 wt.% DI water and weighed down at the corners with glass stoppers to allow the exchange of NMP into the water bath. After 15-45 minutes the membrane was transferred to a final non-solvent bath of 100 wt.% water to fully solvent exchange the pores overnight, also weighed down to submerge fully. The membrane was dried at room temperature. Characterization was performed on pieces cut from the center and most uniform portion of the membrane. The viscosity of the copolymer solutions in NMP was measured at 20 °C using a Brookfield RDV-II Pro viscometer equipped with a small-sample adapter and cylindrical spindle.

CHARACTERIZATION OF MEMBRANES

[0088] A simple estimate of the water flow through the membranes was made by cutting a 47-millimeter (mm) circle of the membrane and placing it on a fritted funnel and clamped. The vacuum filter flask was tared on a balance then 100 g of water was added to the fritted funnel and one atmosphere vacuum was applied for 15-60 min. (minutes). All data were normalized to a 60-min. run time. The water flow was calculated by placing the vacuum filter flask on the tared balance and recording the value.

[0089] The surface porosities and cross-sectional morphologies of the membranes were characterized using Carl Zeiss Supra VP scanning electron microscopy (SEM). The “top” membrane surfaces (those that were first in contact with the NMP/water bath) were imaged for selective surface morphology. The membrane samples were coated with ~0.3 nm Pt/Pd target using Cressington 208 high resolution sputter coater equipped with thickness controller MTM-20. The surface morphology was imaged using low voltage capability (≤ 5 kV, probe current 200

nA and inlens surface sensitive detection mode at 100,000 × magnifications. A minimum of 3 images were combined for digital image analysis using Clemex Vision PE 6.0.035 software to estimate the pore size distributions and pooled for the analysis. Samples for cross-sectional imaging were soaked in ethanol for 5 minutes and cryo-fractured using liquid nitrogen, then allowed to come to room temperature and dried in air. The cryo-fractured membrane samples were coated with Pt/Pd target and imaged using SEM for cross sectional morphology.

[0090] The interaction of the membrane surfaces with water was quantified via measurement of contact angle using a Kruss DA-25 drop shape analysis system. A small square section of membrane was cut out from the center of the membrane, and mounted on a glass microscope slide using double sided tape. A 2-microliter water droplet was deposited on the surface and the drop shape was measured using digital curve fitting 5 times with a 1 second spacing and the resulting contact angles of the water droplet with the membrane surface were averaged together.

EXAMPLES 9-10: MEMBRANES CAST FROM 20/80 MPP-DMP COPOLYMER WITH PS-PEO DIBLOCK COPOLYMER

[0091] A sample of an amphiphilic block diblock copolymer was obtained from Sigma-Aldrich, which is described in their catalog as being comprised of a block of polystyrene (PS) having an Mn of about 30,000 g/mole, which has been coupled to a block of poly(ethylene oxide) (PEO) of Mn of about 1,000 g/mole. From this description we conclude that this PS/PEO block copolymer contains only about 3 wt.% of hydrophilic block by weight. In Examples 9 and 10, solutions containing 16 wt.% of the 20/80 MPP-DMP copolymer of Example 2 were prepared in the presence of 2 and 4 wt.% of the PS/PEO diblock copolymer, respectively, and cast into membranes following the same procedures as described above. The results of SEM image analysis of these membranes are presented in Fig. 1. The surface appearance of the membranes characterized by SEM were found to be very similar to that of Example 6 which was prepared by casting the MPP-DMP copolymer alone.

[0092] The blends of Examples 9-10 containing PS/PEO copolymer yielded membrane surfaces upon phase-inversion casting which had pore size distributions that showed as good or better consistency in pore size distribution as seen for Example 6, which was made from MPP-DMP copolymer alone (Table 5). From this we can conclude that the presence of short blocks of PS has not substantially disrupted the inherently good membrane-forming characteristics of the MPP-DMP copolymer. The contact angle of the membranes containing the PS-PEO diblock as additive show a slight trend towards reduced contact angle, and a decrease in Tg which most likely results from forming a miscible blend between the MPP-DMP copolymer and the PS blocks. It is expected that this type of additive will not be soluble in NMP/water, contrary to

PVP, and so it would be expected to be present in the membrane itself. Given the low level of PEO in the PS/PEO diblock copolymer, it is not surprising that the contact angle was only slightly reduced relative to Example 6.

Table 5. Properties of Membranes Made from Blends of MPP-DMP Copolymer and PS/PEO Diblock Copolymer

Ex. No.	Wt% Polymer In NMP Casting Dope	Surface Pore Size Distribution of Membrane (μm)	Membrane Tg ($^{\circ}\text{C}$)	Water Contact Angle
6	16% Ex. 2	12.2 ± 3.8	210	86
9	16% Ex. 2 + 2% PS-PEO	10.1 ± 2.0	183	84
10	16% Ex. 2 + 4% PS-PEO	9.2 ± 1.7	176	80

PREPARATIVE EXAMPLES 11-13: PREPARATION OF MPP-DMP COPOLYMERS WITH 20, 50, AND 80 MOLE PERCENT MPP

[0093] MPP-DMP copolymers with 20, 50, and 80 mole % MPP were prepared in a 1-gallon reactor using the same methods as in Preparative Examples 2-4. The dried copolymers were characterized for molecular weight distribution as described above for Preparative Examples 2-4. The results for Preparative Examples 11-13 are summarized in Table 6.

Table 6. Characterization of MPP-DMP Copolymers of Preparative Examples 11-13

Ex. No.	MPP/DMP (mole/mole)	GPC Mn (g/mole)	GPC Mw (g/mole)	GPC D (Mw/Mn)	IV in CHCl_3 (dL/g)
11	20/80	63,010	210,800	3.3	1.14
11a	20/80	49,940	199,700	4.0	1.08
12	50/50	42,460	216,200	5.1	0.98
13	80/20	36,490	310,700	8.5	1.08

EXAMPLES 14-16: CASTING OF MEMBRANES VIA SOLVENT/NON-SOLVENT PHASE INVERSION PROCESS

[0094] Membranes were cast using the same procedures as described for Examples 5-10, except that the temperature was controlled to be 35°C throughout the casting and initial phase-inversion coagulation process. The vials of copolymer solutions in NMP were equilibrated for several hours in a milled aluminum “dry block” which was controlled at $35.0 \pm 0.1^{\circ}\text{C}$ by use of an electric heater. The glass casting plates and casting knife were equilibrated for several hours atop an electrically-heated hot plate at $35.0 \pm 0.1^{\circ}\text{C}$ before use. The NMP/water coagulation solution of 2 liters was contained in a digitally-controlled thermostat bath at $35.0 \pm 0.1^{\circ}\text{C}$. Additionally the viscosity of the copolymer solutions in NMP was measured using a Brookfield LVDV3T viscometer equipped with a cone & plate measuring heat and circulating water bath, controlled to within 0.1°C of the desired temperature.

[0095] Membranes were cast at 35°C and characterized for surface pore size distribution and cross-sectional structure by SEM, and the results are summarized in Table 7 and in Fig. 4. The solution viscosity shows a trend towards lower viscosity as MPP co-monomer content is

increased. A strong correlation between the amount of MPP co-monomer and the formation of macrovoids in the cross-section of the membranes is also observed.

Table 7. Membranes cast from MPP-DMP copolymers into 30/70 NMP/water at 35 °C

Ex. No.	NMP Casting Dope		Membrane Properties		
	Wt% Resin	Viscosity (cP at 35°C)	Surface Pore Size Distribution (nm)	Surface Pore Density (pores per μm^2)	Extent of Macrovoid Formation
14	16% Ex. 11	6,838	11.4 $\pm$ 3.0	508	Very low
15	16% Ex. 12	1,474	10.4 $\pm$ 2.4	607	Moderate
16	16% Ex. 13	909	9.7 $\pm$ 1.9	476	High

EXAMPLE 17 AND COMPARATIVE EXAMPLE 2: COMPARISON OF PES/PVP AND 50/50 MPP-DMP MEMBRANES

[0096] To facilitate comparison, the membrane of Example 17 was prepared using the 50/50 MPP-DMP copolymer of Example 12 and the procedure of Example 15, except that the concentration of the copolymer was increased to 18% by weight in order to better match the expected viscosity of Comparative Example 2.

[0097] The solution viscosities measured at 20°C of Comparative Example 2 and Example 17 were similar but not quite as high as stated in Table 9 of International Application Publication WO 2013/131848. Because the membrane castings were to be conducted at 35°C, the solution viscosities were measured at that temperature and the viscosity of Example 17 was found to be significantly higher than the Comparative Example 2. Because of differences in the temperature sensitivity between a PES/PVP blend and a single MPP-PPE copolymer in NMP, no further adjustments to solution viscosity were made.

[0098] Flat membranes were cast from these solutions at 35°C according to the procedure of Example 1 in the '848 application. The dried membranes were characterized by SEM, the results of which are shown in Fig. 2. The characteristics of the membranes are provided in in Table 8. The membranes of Comparative Example 2 have a much higher degree of macrovoid formation, larger mean surface pore sizes and lower pore density than those of Example 17.

Table 8. Flat Membranes Cast According to the Conditions of the '848 Application.

Ex. No.	NMP Casting Dope			Membrane		
	Wt% Resin	Viscosity (cP at 20°C)	Viscosity (cP at 35°C)	Surface Pore Size Distribution (nm)	Surface Pore Density (pores per μm^2)	Extent of Macrovoid Formation
C2	14% 6020P / 5% K30 / 2% K90 / 3% H ₂ O	5,764	1,858	11.3 $\pm$ 3.0	1,803	High
17	18% Ex. 12	4,386	3,270	9.9 $\pm$ 2.1	2200	Moderate

EXAMPLES 18-20 AND COMPARATIVE EXAMPLE 3: HOLLOW FIBER SPINNING

[0099] The membrane-forming compositions (NMP casting dopes) of Examples 14-16, (containing the MPP-DMP copolymers of Examples 11-13, respectively) and Comparative Example 2 were processed into hollow fiber membranes according to the methods disclosed in the '848 application. ULTRASON™ E 6020 P (BASF) was maintained for 24 hrs. under vacuum prior to mixing to remove all moisture. The chemicals were mixed in a glass bulb until a homogenous solution was reached. Before filling the spinning solution into the spinning set up, the composition was filtered through a 25 µm metal mesh to remove any residual particles in the composition. The spinning solution was degassed for 24 hrs. before the spinning. For all spinnings, a bore solution of 70 wt% deionized water and 30 wt% NMP was prepared and was degassed for 24 hrs. before use.

[0100] Hollow fiber membranes of PES and PVP (Comparative Example 3) were prepared on a laboratory scale by dry-wet immersion precipitation spinning using the apparatus shown in the schematic of Fig. 3 and under conditions adapted from the '848 application. The copolymer solution along with the bore liquid were simultaneously pumped through a double orifice spinneret and after passing the air gap, immersed into the water coagulation bath. The take-up velocity was controlled by a pulling wheel, which enabled also stretching of the fiber. A solution of MPP-DMP copolymer according to Example 12 of 18% by weight in NMP was successfully spun into hollow PPE fibers to produce Example 18 using the same apparatus and the same conditions as used to prepare Comparative Example 3.

[0101] A summary of the fiber spinning conditions, spinneret geometry, and measured dimensions of the dried hollow fibers is shown in Table 9. For Comparative Example 3, the rinsing bath was held at 65 °C according to the example in the '848 application, which is understood to be for rinsing away excess PVP from the surface of the hollow fiber membrane. For Examples 18-20, which were prepared from the 20/80, 50/50, and 80/20 MPP-PPE copolymers, respectively, the rinsing bath was held at 30 °C for safety in handling the fibers and because there is no PVP to be washed away. The take-up velocity was adjusted such that the wall thickness of the two hollow fiber samples was in the range of 40-60 micrometers. The post treatment process for the hollow fiber produced was as described in the '848 application. The fibers were washed in 70 °C purified water for 3 hrs. After 1.5 h the water was exchanged. Afterwards the fibers were rinsed for another 24 hrs. in water at tap temperature. After the rinsing step, the fibers were hung in the lab to dry in air at ambient temperature.

[0102] Based on the finding that the membrane-forming polymer solution viscosity in NMP was very sensitive to the amount of MPP co-monomer in the copolymer, the concentration of each resin was adjusted so as to yield an essentially constant solution viscosity of just over

3,000 cP. As a result there is a direct correlation between the level of MPP co-monomer in the copolymer and the mass of PPE per unit length of fiber, with Example 18a demonstrating the most efficient use of resin under the same spinning conditions. The fiber wall thickness was also maintained to a greater extent in Example 19, suggesting that with further optimization of fiber spinning conditions to reduce the wall thickness, a greater reduction in mass per unit length can be realized.

Table 9. Summary of Process Conditions for Hollow Fiber Spinning and Fiber Properties

	C. Ex. 3	Ex. 18	Ex. 19	Ex. 20
Wt% resin in NMP casting dope	14% 6020P / 5% K30 / 2% K90 / 3% H2O	18% Ex. 12	14% Ex. 11	20% Ex. 13
Viscosity (cP at 35 °C)		3270	3091	3137
Dope temp. [°C]	35	35	35	35
Die temp. [°C]	-	-	-	-
Shaft temp. [°C]	~22	~30	~30	~22
Shaft humidity [%]	50	60	60-65	60
Room humidity [%]	35	40	40	40
1 st bath temp. [°C]	30	30	30	30
2 nd bath temp. [°C]	65	30	30	30
Air Gap [cm]	100	100	100	100
Dope extrusion rate [mL/min]	1.56	1.56	1.56	1.56
Bore extrusion rate [mL/min]	3.1	3.1	3.1	3.1
Take up velocity [m/min]	9.12	7.04	7.07	7.00
Spinneret dimensions				
Inner diameter [mm]	0.4	0.4	0.4	0.4
Outer diameter [mm]	1.12	1.12	1.12	1.12
Dry hollow fiber dimensions by SEM				
Inner diameter [μm]	445	605	510	605
Wall thickness [μm]	59	41	47	23
Mass per km (g)	25.9	40.2	31.1	43.3

PREPARATION OF HOLLOW FIBER MEMBRANE MODULES

[0103] Lab scale hollow fiber membrane modules as shown in Fig. 4 were prepared for the clean water flux and molecular weight cut off measurements. 5-10 fibers, depending on the geometry were guided through polypropylene tubes and the t-connections, which provide access to the outer surface of the hollow fibers. Both ends were sealed with hot glue. After the glue hardened, the modules were carefully cut open at one or both ends to expose the inner core of the hollow fibers to make them ready to use. The membrane length was between 25 and 30 cm. The fibers of Example 20 were more brittle than the other fibers, and extra care was required to glue the fibers of Example 20 into the modules to avoid damaging the fibers.

MEASUREMENT OF CLEAN WATER FLUX

[0104] Clean water flux (CWF) was measured as follows. A pump was connected to a mass flow controller and a pressure sensor. Behind the pressure sensor the membrane module was connected so that the filtration direction was inside- out, that is the water was forced into the

bore side of the membrane and permeated through the membrane to the outside of the membrane. The filtration mode was dead end filtration, that is only one end of the filtration module was cut open and connected to the feed solution. The flow rate was set to 100 g/h and the feed pressure was recorded over time. After the pretreatment of the membrane modules, the experiment was run for 1 hr. to achieve steady state conditions.

[0105] Prior to the measurement, all the hollow fibers were wetted with a mixture of 50 wt% water and 50 wt% ethanol. Afterwards clean water was permeated through the hollow fiber membranes for 15 minutes to remove all residual ethanol from the fibers. The measurement was started directly after the pretreatment. The results of the water flux measurements are provided in Table 10.

Table 10. Clean Water Flux Measurements

Ex.	Clean Water Flux (L/(h·m ² ·bar))
CE3 (PES/PVP)	
Module 1	8.0
Module 2	8.6
Module 3	7.9
Module 4	9.1
Average	8.4 ± 0.6
E18 (E12 – 20/80 MPP-DMP)	
Module 1	44.3
Module 2	24.9
Module 3	64.8
Module 4	60.1
Module 5	54.4
Average	49.7 ± 15.8
E19 (E11 – 50/50 MPP-DMP)	
Average of 4 Modules	40.2 ± 21
E20 (E13 – 80/20 MPP-DMP)	
Average of 3 Modules	133 ± 18.5

As can be seen from Table 11, the highest clean water flux (133 L/(h·m²·bar)) was obtained at the highest MPP comonomer content – the 80/20 MPP-DMP copolymer of Example 20.

Without being bound by theory, this effect may be due to the thinner fiber cross-section obtained with those fibers – a wall thickness of only 23 µm, as reported in Table 10. Although the individual values vary, the clean water flux for all the PPE copolymer fibers (Examples 18-20) are substantially higher than the C. Example 3 fiber, which has a clean water flux of about 8 L/(h·m²·bar), and which was taught by prior art application publication '848.

MEASUREMENT OF MOLECULAR WEIGHT CUT-OFF

[0106] Prior to the measurement of the molecular weight cut-off (MWCO), all membrane modules were wetted with a mixture of 50 wt% water and 50 wt% ethanol. Next,

clean water was permeated through the hollow fiber membranes for 15 minutes to remove all residual ethanol from the fibers. The measurement was started directly after the pretreatment.

[0107] Fig. 5 shows a schematic drawing of the MWCO measurement apparatus. Both ends of the hollow fiber filtration modules shown in Fig. 4 were cut and the feed solution was pumped through the inside of the hollow fibers and the retentate recirculated to the feed tank. The permeate solution is circulated across the outside of the fibers via the T-connectors and recycled to a separate feed tank. The cross flow velocity was controlled via the pump and the feed, retentate, and pressure are recorded. The permeate pressure was at ambient pressure. A valve at the retentate side can optionally be used to control the retentate pressure.

[0108] A turbulent flow inside the hollow fiber is desirable in order to prevent concentration polarization during the experiment. To provide turbulent flow, the cross flow velocity is set to target a Reynolds number of about 3000. The Reynolds number is defined according to Equation 1, whereas " η " is defined as the dynamic viscosity of the fluid, " ρ " is defined as the density of the fluid, " v " defined as the fluid velocity and " d " defined as the inner fiber diameter.

$$Re = \frac{\rho * v * d}{\eta} \quad (\text{Eq. 1})$$

[0109] As a feed solution, a mixture of four different dextrans, which differ in molecular weight (1 kDa, 4 kDa, 8 kDa and 40 kDa), was used. The concentration in the feed solution was 0.5 g/L for each dextran. The molecular weight cut off is defined as that molecular weight of a species which is retained up to 90 percent by the membrane. The retention is calculated by comparing the gel permeation chromatography of the initial solution of dextrans to that measured on permeate and retentate solutions after reaching equilibrium.

[0110] Three filtration modules of each of Comparative Example 3 and Examples 18-20 were tested, and the results are summarized in Table 11. For the three PES modules of Comparative Example 3, it was possible to run the MWCO experiment under conditions of a Reynolds number (Re) of 3000. However, no MWCO was determined for two modules (Retention was always below 90 percent for the given feed.) and for the third module the MWCO was not stable over time.

[0111] In contrast to the PES/PVP hollow fibers of Comparative Example 3, the PPE copolymer hollow fibers of Examples 18-20 appeared to be defect-free under the same conditions of high Re (3,000-3,600) and high trans-membrane pressure (TMP, 1.9-3.5 bar) and yielded stable MWCO values of 6-15 kDa. Thus the membranes of Examples 18-20 provide an improved combination of higher CWF and stable low MWCO over the membrane produced from PES and PVP. In addition, the membranes of Examples 18-20 provided improved

mechanical integrity. The fact that this performance can be achieved from membranes formed from inherently hydrophobic PPE resin in the absence of pore-forming additives (hydrophilic polymer), using only a simple wetting process based on aqueous ethanol, is surprising.

[0112] Stable readings were readily obtained for the additional examples: since the MWCO values at either extreme of MPP co-monomer content were essentially the same we conclude that there is no significant effect of this parameter on the ability to form well-controlled pore size distributions from the PPE during hollow fiber spinning.

Table 11. Molecular Weight Cut-off Measurements

Hollow Fiber	Polymer	MWCO (kDa)			
		60 min	75 min	120 min	180 min
CE3	CE2 (PES/PVP)	Re = 3,000; flow = 100 L/h; TMP = 2.1 bar			
		10.1	-	44.3	59.3
		90 Percent retention was not reached.			
		90 Percent retention was not reached.			
E18	E12 (50/50 MPP-DMP)	Re = 3,000; Flow = 140 L/h; TMP = 2.1 bar			
		8.3	7.3	6.3	-
		5.2	6.6	5.3	-
		6.4	5.2	5.2	-
		Average = 5.6			
E19	E11 (20/80 MPP-DMP)	Re = 3,600; Flow = 140 L/h; TMP = 1.9 bar			
		61.7	54.5	51.4	-
		15.9	14.6	13.6	-
		12.8	13.6	13.4	-
		Average = 13.5			
E20	E13 (80/20 MPP-DMP)	Re = 3,250; Flow = 150 L/h; TMP = 3.5 bar			
		16.3	-	16.1	15.6
		14.0	-	13.5	17.5
		17.7	-	19.5	13.2
		Average = 15.4			

SEM COMPARISON OF HOLLOW MORPHOLOGY

[0113] The hollow fibers of Comparative Example 3 and Example 18 were analyzed by SEM, the results of which are shown in Fig. 6. The membranes of Comparative Example 3, prepared from PES and PVP, show a strongly asymmetric cross-sectional morphology, and similar to those obtained for flat membrane castings of the same dope composition (Fig. 6). The dense selective layer appears to be thin for the PES/PVP comparative example in both the flat and the hollow fiber geometry. In comparison, the morphology of the hollow fiber of Example 18 shows a dense, spongy morphology that persists across the hollow fiber cross-section, which is also consistent with the appearance of the flat membranes produced from the same dope composition (Fig. 6). Thus the high-IV PPE co-polymers disclosed herein provide inherently superior membrane-forming characteristics which can be realized in either flat or hollow fiber geometries.

EXAMPLES 21-23: FLAT MEMBRANES MADE FROM 20/80 MPP-DMP COPOLYMER AND HYDROPHILIC POLYMER IN COAGULATION BATH

[0114] In each example, the membrane-forming dope solution contained 14 wt% of the 20/80 MPP-DMP copolymer of Example 14 in NMP. The coagulation bath was 50/50 by weight NMP-water in Example 21. The effect of adding 0.2 wt% of PVP to the coagulation bath, either the low molecular weight K30 grade (Example 22), or the high molecular weight K90 grade (Example 23), was evaluated. (This corresponds to adding the PVP to the bore fluid in hollow fiber spinning, as illustrated by Process “B” in Fig. 7.) The membranes were placed in the coagulation bath for 15 minutes, transferred to a rinse bath of deionized water, and allowed to soak overnight to complete the extraction of residual NMP from the membrane. The membranes were then dried for 24 hrs. in a stream of dry nitrogen.

[0115] The diameter and frequency of the pores on the upper surface (selective layer corresponding to the inner surface of hollow fibers) of the dry membranes were characterized using SEM according to the procedure described above. Contact angle of the dried membranes was also measured. As a more stringent test of the degree to which PVP was attached to the surface of the membranes, small strips of the dry membrane were immersed in water and soaked for 3 hours at 70 °C, dried overnight, and measured again for contact angle. The results are summarized in Table 12, and SEM images of the porous surfaces of Examples 21a, 21b, and 21c are depicted in Fig. 8. The contact angle of the membranes prepared in Example 21 without any additive in the coagulation bath exhibit a high contact angle as expected from a hydrophobic polymer. By addition of only a low concentration of a hydrophilic additive such as PVP to the coagulation bath in Example 22 and 23, the contact angle is reduced by a significant amount, and this effect persists even after soaking in hot water. The apparent ability of the high molecular weight DMP-MPP copolymer to “trap” the additive on the membrane surface during the phase-inversion process is surprising. The improvement of this process of our invention in utilizing the hydrophilic additive is readily apparent against the conventional use of PVP to make the membrane of Comparative Example 1, Table 4.

Table 12. Properties of Membranes Made from MPP-DMP Copolymers and Hydrophilic Polymer in Coagulation Bath

Ex.	Polymer Additive in Coagulation Bath	Surface Pore Size Distribution (nm)	Surface Pore Density (pores per μm^2)	Contact Angle dry, as cast	Contact Angle after 3 hrs. in 70°C water, then drying
21a	none	10.6 ± 2.7	1863	98.9 ± 1.1	88.9 ± 7.0
21b	none	10.6 ± 2.5	1507		
22a	0.2% PVP K30	10.7 ± 2.7	418	56.3 ± 4.8	65.2 ± 5.6
22b	0.2% PVP K30	10.7 ± 2.4	1009		
23a	0.2% PVP K90	11.0 ± 2.6	1144	62.4 ± 1.3	53.3 ± 3.5
23b	0.2% PVP K90	10.0 ± 2.1	406		

[0116] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) is to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. “Or” means “and/or.” The endpoints of all ranges directed to the same component or property are inclusive and independently combinable. Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group. All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. The terms “first” and “second” and the like, as used herein do not denote any order, quantity, or importance, but are only used to distinguish one element from another. The term “comprises” as used herein is understood to encompass embodiments consisting essentially of, or consisting of, the named elements.

[0117] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0118] As used herein, the term “hydrocarbyl” refers broadly to a substituent comprising carbon and hydrogen, optionally with 1 to 3 heteroatoms, for example, oxygen, nitrogen, halogen, silicon, sulfur, or a combination thereof. Unless otherwise indicated, each of the foregoing groups can be unsubstituted or substituted, provided that the substitution does not significantly adversely affect synthesis, stability, or use of the compound. The term “substituted” as used herein means that at least one hydrogen on the designated atom or group is replaced with another group, provided that the designated atom’s normal valence is not exceeded. When the substituent is oxo (i.e., =O), then two hydrogens on the atom are replaced. Combinations of substituents and/or variables are permissible provided that the substitutions do not significantly adversely affect synthesis or use of the compound. All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0119] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

CLAIMS

1. A method of making a porous asymmetric membrane, wherein the method comprises:

dissolving a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, a polyethersulfone, a polysulfone, a polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate), or a combination comprising at least one of the foregoing in a water-miscible polar aprotic solvent to provide a membrane-forming composition; and

phase-inverting the membrane-forming composition in a first non-solvent composition comprising

water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and

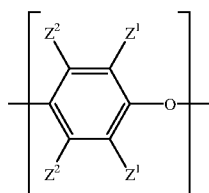
a polymer additive dissolved in the first non-solvent composition,

to form the porous asymmetric membrane.

2. The method of claim 1, further comprising washing the porous asymmetric membrane in a second non-solvent composition.

3. The method of claim 1 or 2, further comprising drying the porous asymmetric membrane.

4. The method of any of claims 1-3, wherein the hydrophobic polymer comprises a poly(phenylene ether) copolymer comprising first and second repeat units independently having the structure:



wherein each occurrence of Z^1 is independently halogen, unsubstituted or substituted C_1 - C_{12} hydrocarbyl provided that the hydrocarbyl group is not tertiary hydrocarbyl, C_1 - C_{12} hydrocarbylthio, C_1 - C_{12} hydrocarbyloxy, or C_2 - C_{12} haloalkoxy, wherein at least two carbon atoms separate the halogen and oxygen atoms;

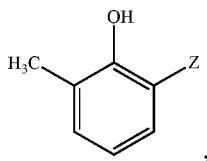
wherein each occurrence of Z^2 is independently hydrogen, halogen, unsubstituted or substituted C_1 - C_{12} hydrocarbyl provided that the hydrocarbyl group is not tertiary hydrocarbyl, C_1 - C_{12} hydrocarbylthio, C_1 - C_{12} hydrocarbyloxy, or C_2 - C_{12} haloalkoxy, wherein at least two carbon atoms separate the halogen and oxygen atoms; and

wherein the first and second repeat units are different.

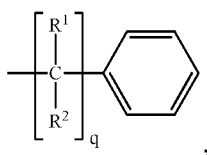
5. The method of any of claims 1-4, wherein the hydrophobic polymer comprises a poly(phenylene ether) copolymer comprising:

80 to 20 mole percent repeat units derived from 2,6-dimethylphenol; and

20 to 80 mole percent repeat units derived from a first monohydric phenol having the structure



wherein Z is C₁-C₁₂ alkyl or cycloalkyl, or a monovalent radical having the structure



wherein q is 0 or 1, and R¹ and R² are independently hydrogen or C₁-C₆ alkyl;

wherein the poly(phenylene ether) copolymer has an intrinsic viscosity of 0.7 to 1.5 deciliters per gram, measured in chloroform at 25 °C.

6. The method of any of claims 1-5, wherein the polymer additive comprises poly(vinyl pyrrolidone), poly(oxazoline), poly(ethylene glycol), poly(propylene glycol), a poly(ethylene glycol) monoether or monoester, a poly(propylene glycol) monoether or monoester, a block copolymer of poly(ethylene oxide) and poly(propylene oxide), polystyrene-*graft*-poly(ethylene glycol), polystyrene-*graft*-poly(propylene glycol), polysorbate, cellulose acetate, glycosaminoglycans such as heparin or heparin sulfate, or a combination comprising at least one of the foregoing.

7. The method of any of claims 1-6, wherein the polymer additive comprises an amphiphilic block copolymer comprising a hydrophobic block and a hydrophilic block.

8. The method of claim 7, wherein the hydrophobic block comprises polystyrene and the hydrophilic block or graft comprises poly(N,N-dimethylacrylamide) or poly(4-vinylpyridine).

9. The method of any of claims 1-8, wherein the first non-solvent composition comprises 10 to 100 weight percent water and 0 to 90 weight percent N-methyl-2-pyrrolidone, based on the total weight of the first non-solvent composition.

10. The method of claim 1, wherein:

the hydrophobic polymer comprises a poly(phenylene ether) copolymer comprising 80 to 20 mole percent repeat units derived from 2,6-dimethylphenol and 20 to 80 mole percent repeat units derived from 2-methyl-6-phenylphenol;

the water-miscible polar aprotic solvent is N-methyl-2-pyrrolidone; and

the polymer additive comprises poly(vinylpyrrolidone), poly(styrene-*co*-vinylpyrrolidone), polystyrene-*block*-poly(N,N-dimethylacrylamide), or a combination comprising at least one of the foregoing.

11. A porous asymmetric membrane made by the method of any of claims 1-10.
12. The porous asymmetric membrane of claim 11, having a contact angle of 40 to 80 degrees.
13. A separation module comprising the porous asymmetric membrane of claim 11 or 12.
14. A method of making a hollow fiber by coextrusion through a spinneret comprising an annulus and a bore, wherein the method comprises coextruding:
 - a membrane-forming composition comprising a hydrophobic polymer comprising a poly(phenylene ether), poly(phenylene ether) copolymer, polyethersulfone, polysulfone, polyphenylsulfone, polyimide, polyetherimide, polyvinylidene fluoride, poly(methyl methacrylate) or a combination comprising at least one of the foregoing, through the annulus, and
 - a first non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, and a polymer additive dissolved in the first non-solvent composition, through the bore,
 - into a second non-solvent composition comprising water, a water-miscible polar aprotic solvent, or a combination comprising at least one of the foregoing, to form the hollow fiber.
15. The method of claim 14, further comprising washing the hollow fiber in a third non-solvent composition.
16. The method of claim 14 or 15, further comprising drying the hollow fiber.
17. A hollow fiber made by the method of any of claims 14-16.
18. The hollow fiber of claim 17, wherein the hollow fiber has a substantially non-porous surface layer.
19. A separation module comprising the hollow fiber of claim 17 or 18.

SEM OF MEMBRANE SURFACES 100,000x

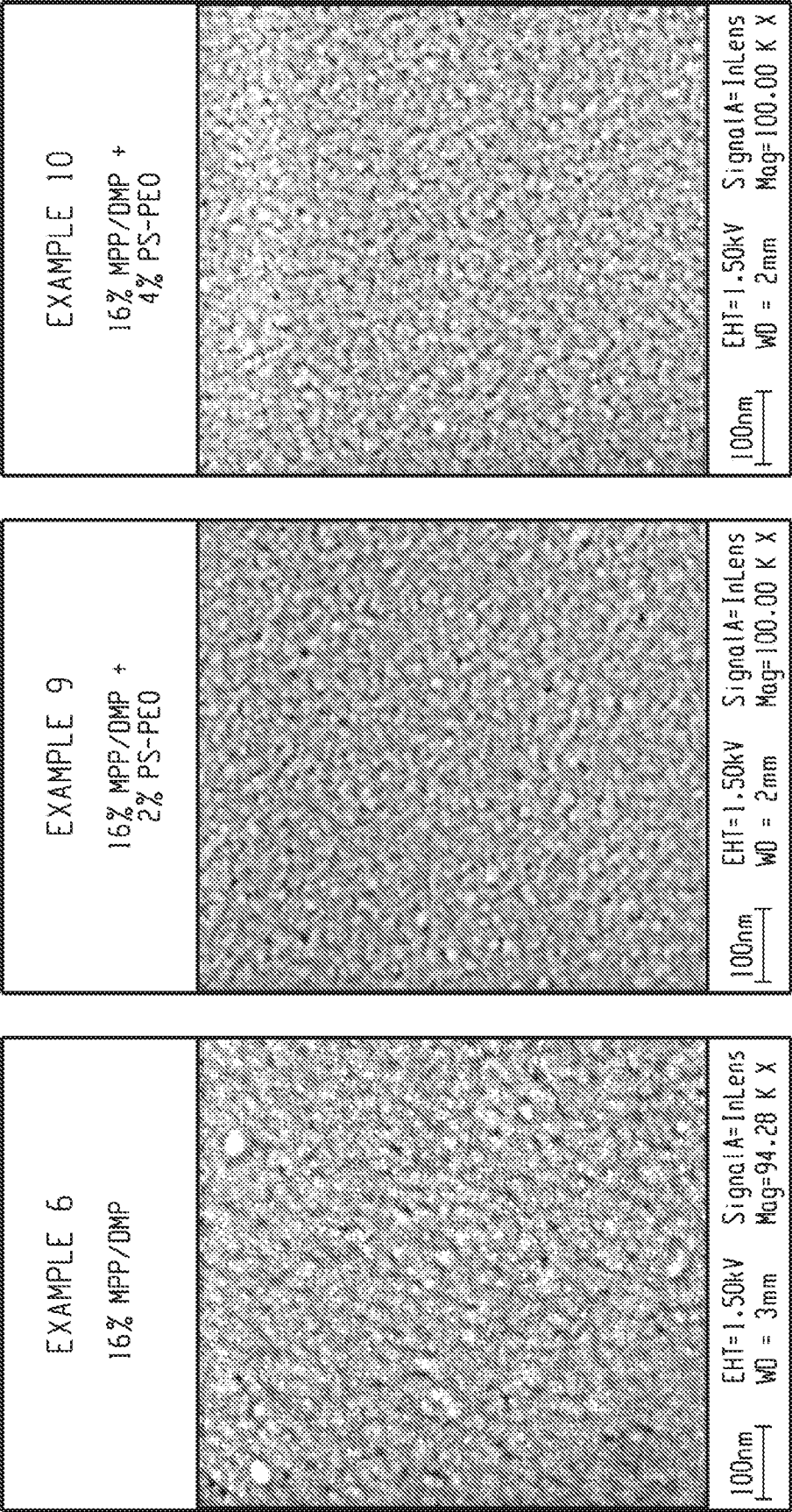
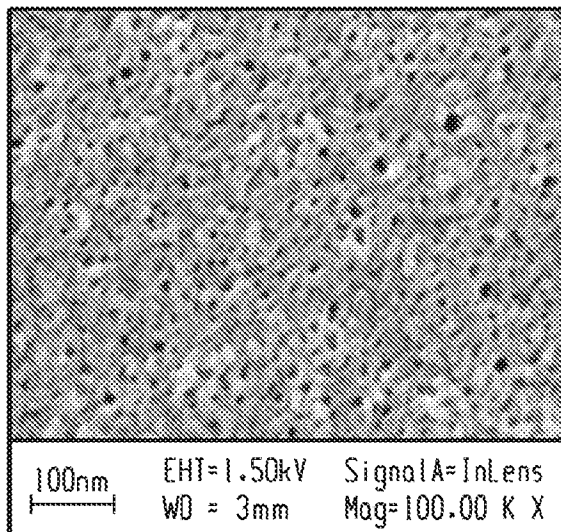


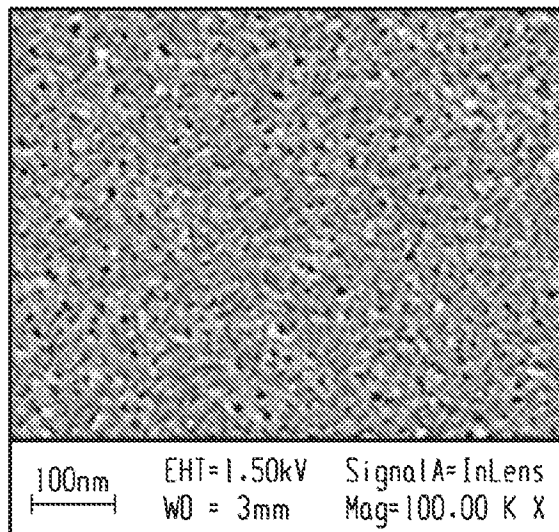
Fig. 1

SEM OF MEMBRANE SURFACES:

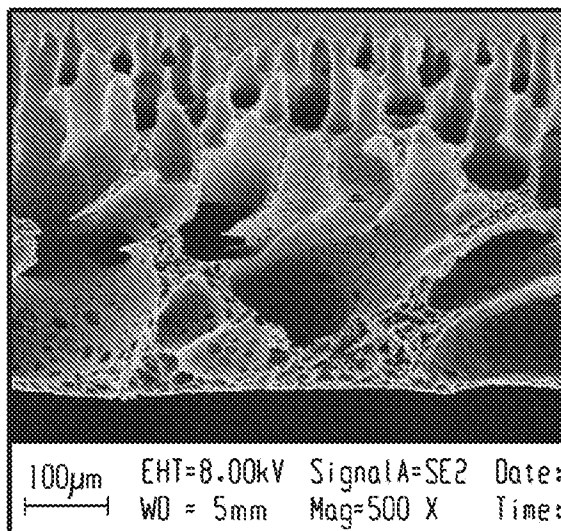
COMPARATIVE EXAMPLE 2

14% 6020P / 5% K30 / 2%
K90 / 3% H₂O IN NMP

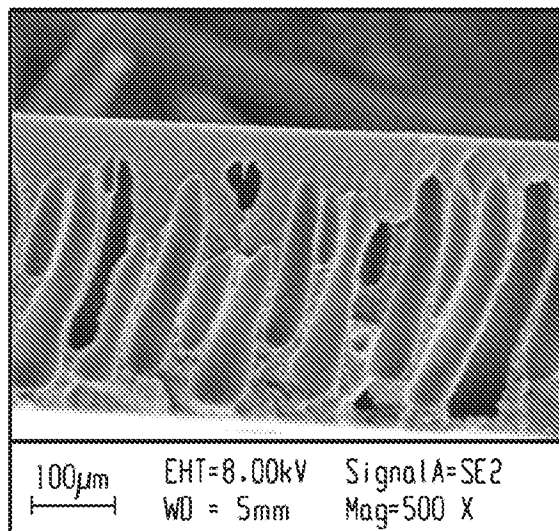
EXAMPLE 17

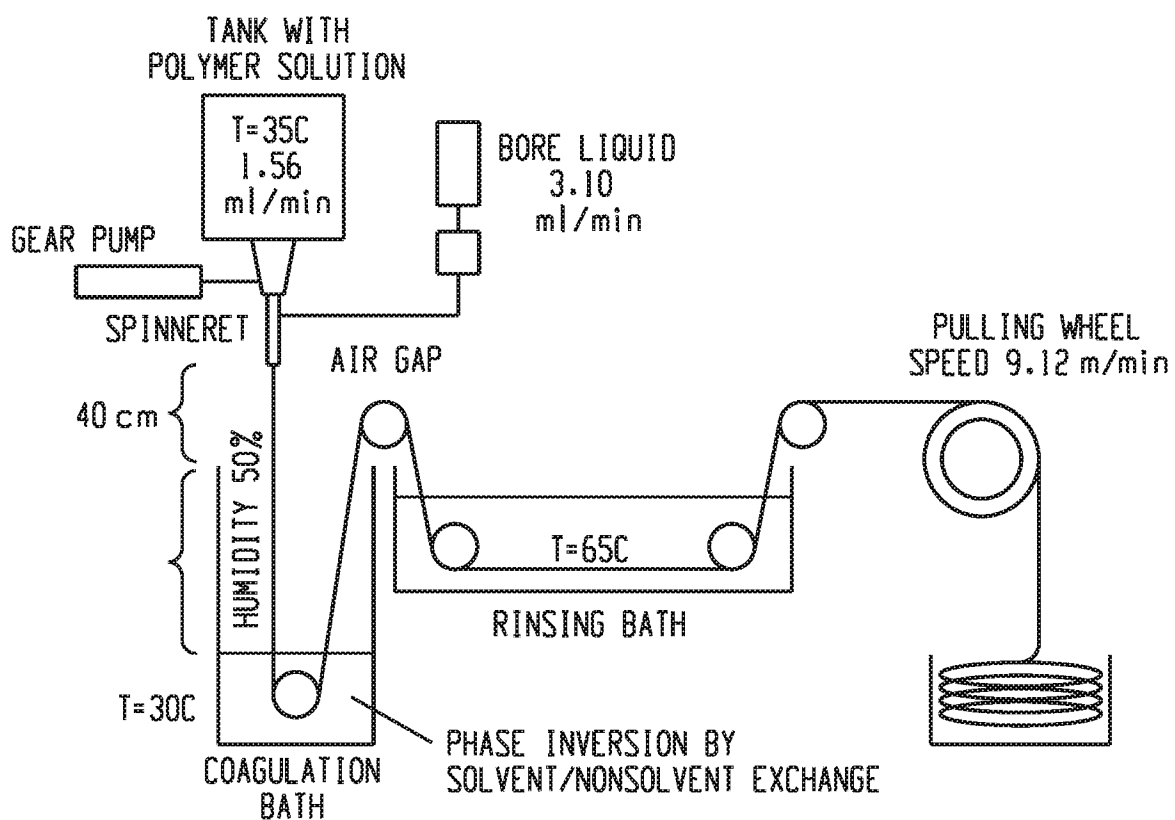
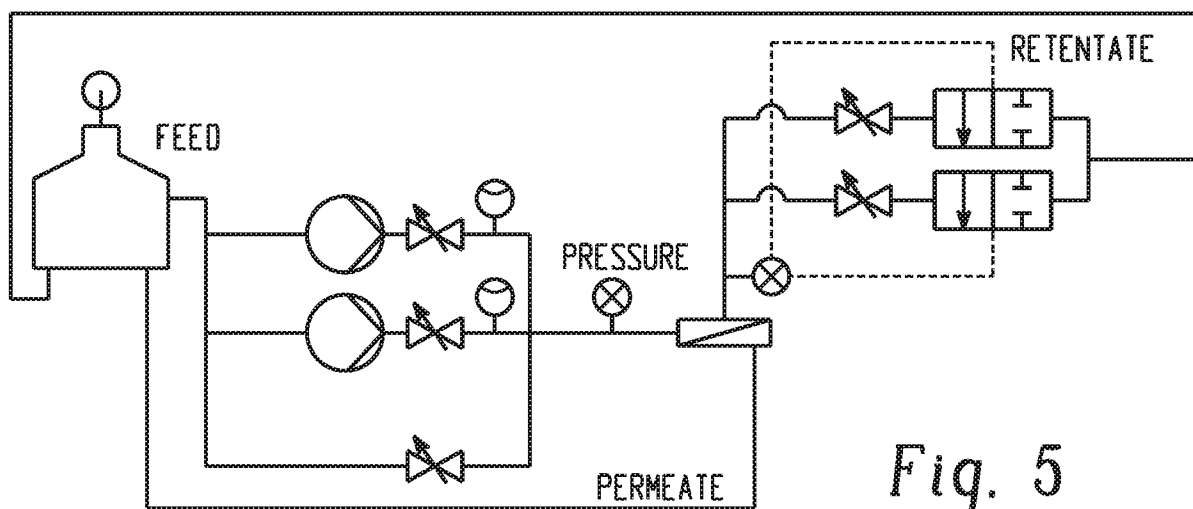
50/50 MPP/OMP
18% IN NMPSEM OF MEMBRANE CROSS-SECTIONS:

COMPARATIVE EXAMPLE 2

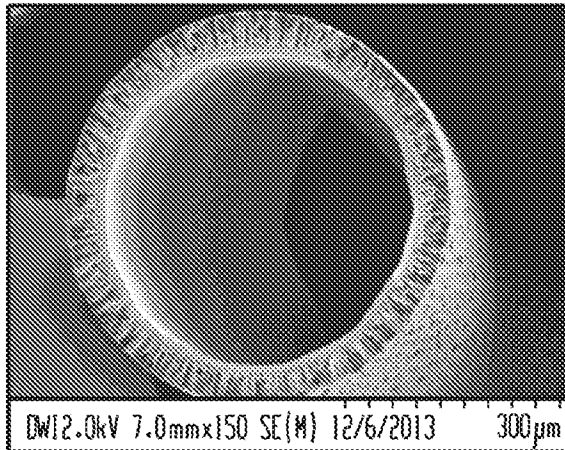


EXAMPLE 17

*Fig. 2*

*Fig. 3**Fig. 4**Fig. 5*

COMPARATIVE EXAMPLE 3
FIBER SPUN FROM DOPE SOLUTION
OF 14% 6020P / 5% K30 / 2% K90 /
3% H₂O / 76% NMP



EXAMPLE 18
FIBER SPUN FROM DOPE SOLUTION
OF 18% EX. 12 / 82% NMP

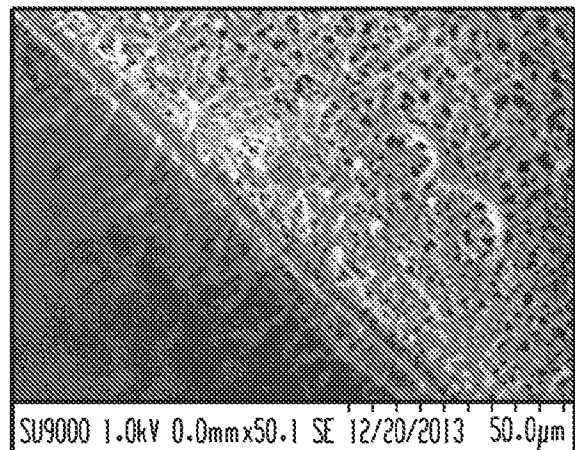
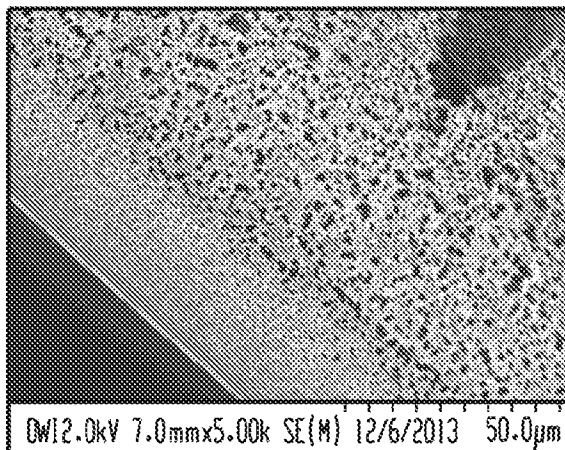
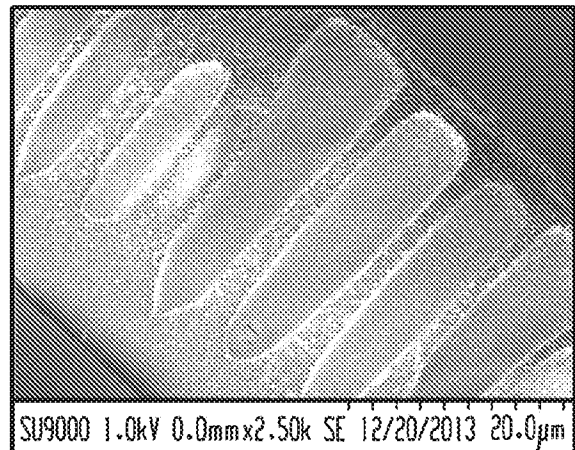
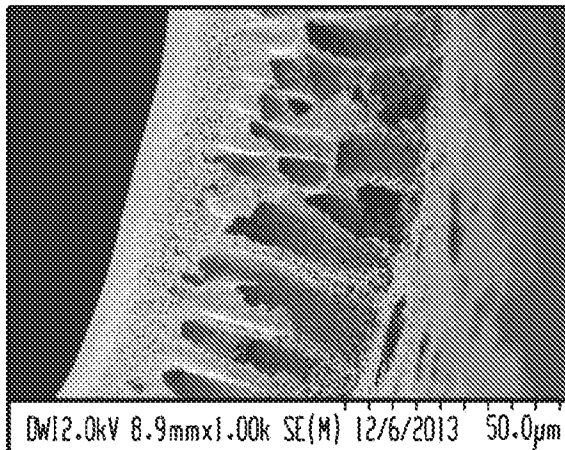
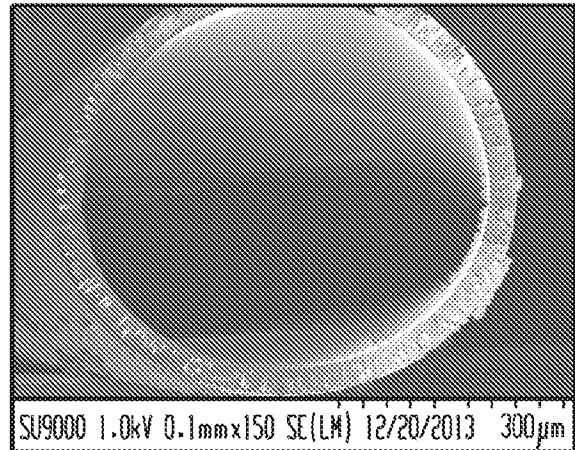


Fig. 6

Fig. 7

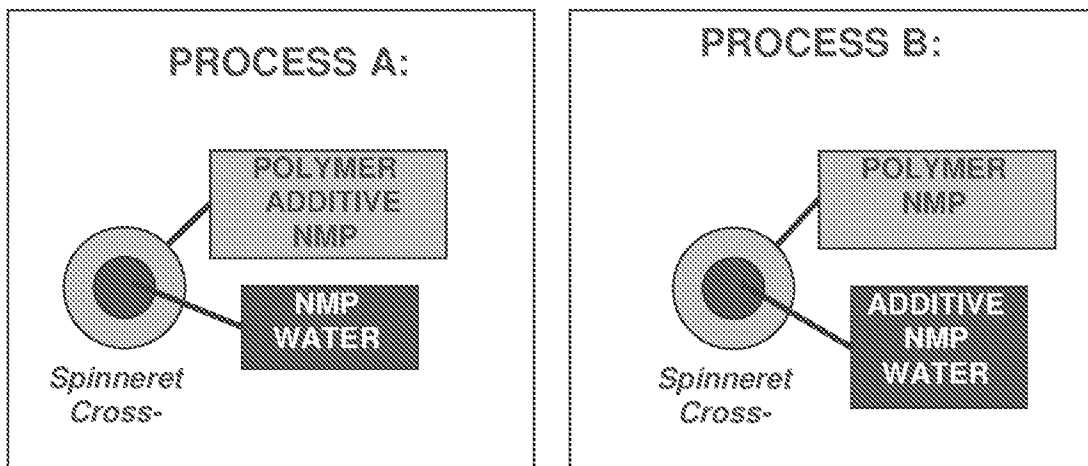
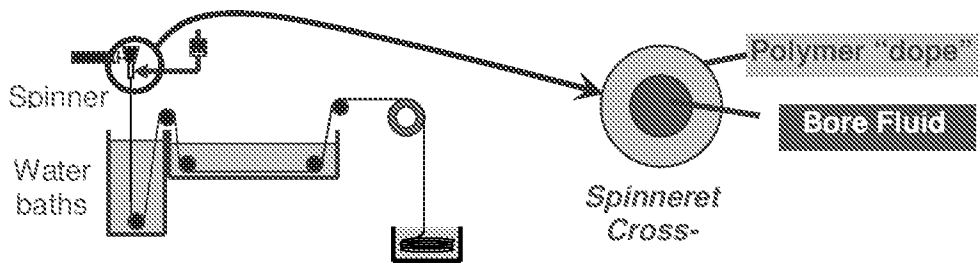
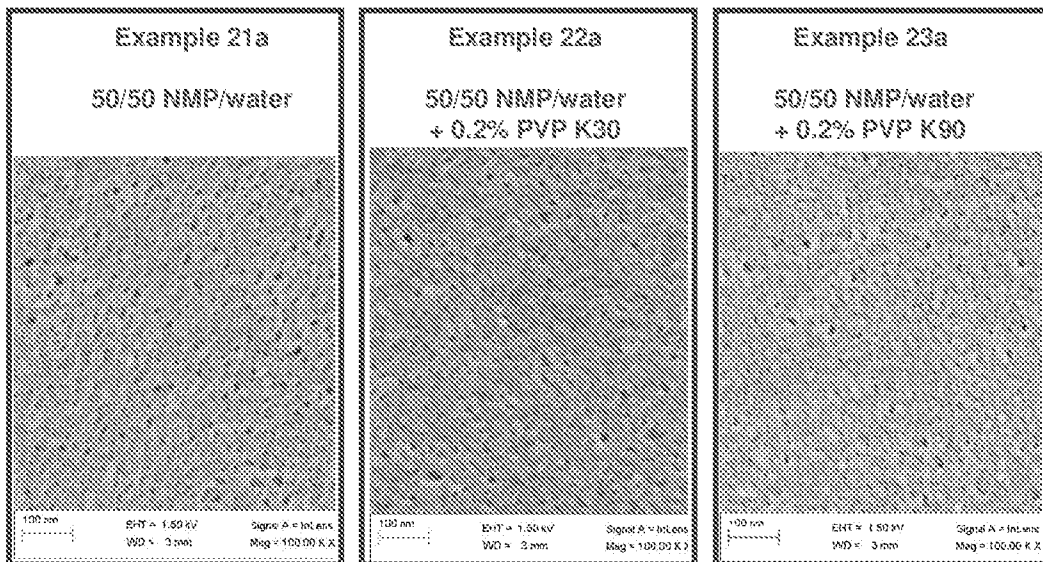


Fig. 8

SEM of membrane surfaces 100,000x



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/028951

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D67/00 B01D71/52 B01D71/76
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 918 019 A1 (ASAHI CHEMICAL IND [JP]) 7 May 2008 (2008-05-07)	11-13, 17-19
Y	abstract paragraphs [0001], [0008], [0011] - [0014], [0034] claims 1,3,18,21-24 figures 1-9	1-10, 14-16
X	EP 0 568 045 A1 (KURARAY CO [JP]) 3 November 1993 (1993-11-03)	11-13, 17-19
Y	abstract page 4, lines 30-50 page 7, line 29 - page 8, line 3	1-10, 14-16
	----- -/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

21 July 2016

Date of mailing of the international search report

29/07/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Lançon, Eveline

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/028951

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2008/207822 A1 (YEAGER GARY WILLIAM [US] ET AL) 28 August 2008 (2008-08-28) abstract paragraphs [0007], [0009], [0016], [0017], [0034], [0082], [0089] -----	11-13, 17-19 1-10, 14-16
X A	WO 2013/131848 A1 (GAMBRO LUNDIA AB [SE]) 12 September 2013 (2013-09-12) cited in the application the whole document -----	11-13, 17-19 1-10, 14-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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