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POLYSULFONE HOLLOW FIBER GAS SEPARATION MEMBRANES WITH IMPROVED PERMSELECTIVITY

FIELD OF THE INVENTION

This invention relates to hollow fiber membranes, their preparation and use in the
5 field of high performance gas separations.

BACKGROUND OF THE INVENTION

The key to the successful development of membranes for gas separation is the
fabrication of membranes with high separation performance by a convenient and
economical method. To achieve selective separation, the membrane must exhibit less
10 resistance to the transport of one or more gases than that of at least one other gas of the
mixture. Thus, selective separation can provide preferential depletion or concentration of
one or more desired gases in the mixture with respect to at least one other gas and therefore
provide a product having a different proportion of the one or more desired gases to the at
least one other gas than that proportion in the original mixture.

15 Ideally a gas separation membrane will possess all of the following properties (as
described in I. Pinnau, Polymers for Advanced Technologies, Vol. 5, No.11 (1994) 733):
high selectivity for a given gas pair (e.g. H_2/N_2 , H_2/CH_4 , He/CH_4 , CO_2/CH_4 , O_2/N_2 , etc.)
and high gas flux for the faster permeable component; good thermal and mechanical
stability; good chemical resistance, particularly against small amount of potential
20 contaminants present in gas streams; long membrane working life; good reproducibility of
the membranes fabricated; and, simple, easy, and economically viable methods of
manufacture.

Of the above criteria, selectivity, temperature resistance and chemical resistance are
mainly determined by the membrane material, whereas other criteria depend not only on
25 the membrane material, but also on the membrane making process. Based on gas transport
through dense polymer membranes, the gas permeation flux is directly proportional to the
permeability coefficient of the polymer material, the pressure difference across the
membrane and the membrane area, and inversely proportional to the separating layer
thickness. The goals in membrane fabrication are to reduce the separating layer thickness,

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to increase the membrane area, as well as to improve the mechanical strength of the membrane.

A hollow fiber membrane can provide the largest membrane area per unit packing volume among the different types of membranes. Composite membranes, asymmetric membranes and multicomponent asymmetric membranes provide a very thin separating layer. Therefore, the development of hollow fiber membranes with an ultrathin separating layer has attracted great attention in all gas separation processes. Although the development of a process for preparing a composite membrane with an ultrathin separating layer is important, especially when expensive polymers are used, the formation of a “defect-free” ultrathin composite hollow fiber membrane is still an extremely difficult task. Successful development of strategies for the fabrication of ultrathin-skinned asymmetric hollow fiber membranes or multicomponent asymmetric hollow fiber membranes from highly selective, existing commercial glass polymers, such as polysulfone, polyethersulfone, polyetherimide, polyimide and new advanced custom-made materials would be a major breakthrough in gas separation technology.

Asymmetric membranes are attractive because they can potentially form an ultrathin separating layer. The method for producing this kind of membrane by an immersion phase inversion process was first disclosed by Loeb and Sourirajan, U.S. Pat. 3,133,132 which is hereby incorporated by reference. These asymmetric membranes were used in industrial liquid separation processes such as reverse osmosis and ultrafiltration. However, these membranes prepared from non-cellulose polymers often exhibit poor selectivity for gas separation due to the presence of excessively large pores on the dried membrane surface and the transport of gas is largely due to Knudsen flow and viscous flow.

Asymmetric hollow fiber membranes are usually prepared by the Loeb-Sourirajan dry/wet or the wet phase inversion process. There are five major steps involved in preparing asymmetric hollow fiber gas separation membranes: (1) preparation of a polymer dope for spinning, (2) spinning of the nascent hollow fiber, (3) coagulation of the nascent fiber with a coagulant, (4) washing and drying, and (5) post-treatment. The formation of asymmetric hollow fiber membranes involves complicated solution thermodynamics and phase inversion kinetics induced by the diffusion of liquid components. Thus, the

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membrane morphology and its performance are affected by many factors.

U. S. Pat. 4,230,463 issued to Henis and Tripodi describes a method for sealing the large pores by coating a thin silicone rubber film on the surface of the asymmetric membranes. The separation properties of these composite asymmetric membranes are generally determined by the material of the asymmetric membrane as opposed to the material of the coating. Coated asymmetric membrane technology has since progressed to the point that hydrogen recovery is performed commercially on a large scale.

U. S. Pat. 4,871,494 issued to Kesting et al. describes a process for forming asymmetric gas separation hollow fiber membranes having graded density skins. This process comprises dissolving a hydrophobic polymer in a solvent system consisting of 1:1 Lewis acid/Lewis base complexes wherein the Hildebrand parameters of the solvent system and the polymer are within less than $1.5 \text{ cal}^{0.5}/\text{cm}^{1.5}$. The useful acids employed as additives must have a Gutmann Acceptor Number (AN) of $47 < \text{AN} < 53$, and the infra-red frequency shifts ($\Delta\nu$) of its forming complex with N-methyl-2-pyrrolidone falling within the range of $-25 < \Delta\nu < -38 \text{ cm}^{-1}$. The solubility parameters of useful acids have been found to have values of $12 < \delta < 12.5 \text{ cal}^{0.5}/\text{cm}^{1.5}$. The polymer dope has a high polymer concentration ($>35\text{wt}\%$), high viscosity ($>100,000\text{cp}$ at 70°C) and a low coagulation value ($0 < G_v < 1.5\text{g}$). The Lewis acids used include acetic acid, propionic acid, butyric acid, isobutyric acid, 2-chloropropionic acid, glutaric acid, sulfuric acid, glycerol, ethylene carbonate, formamide, N-methylformamide, and triethylacetamide. However, very few acids listed other than propionic acid are useful as the efficient additives to make high performance gas separation membranes. The Lewis bases are N-methylpyrrolidone, dimethylformamide, dimethylacetamide, N-formylpiperidine and dimethylsulfoxide. In spinning these hollow fiber membranes, water was used as both the internal and external coagulant.

U.S. Pat. 4,992,221 issued to Malon et al. discloses a process for preparing asymmetric polysulfone hollow fibers with improved selectivity and mechanical strength. The gas separation membranes were produced from a process utilizing polymer dopes having solvent systems formulated from two non-solvents and one solvent. The nonsolvents were chosen according to the nonsolvent strength, i.e. one strong nonsolvent and one weak nonsolvent which were combined with the solvent in an acid:base complex

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solvent system. A strong nonsolvent is defined as one having a $\Delta\delta$ ($\delta_{\text{nonsolvent}} - \delta_{\text{polymer}}$) $\geq 6 \text{ cal}^{0.5}/\text{cm}^{1.5}$. A weak nonsolvent is defined as one with a $\Delta\delta < 6 \text{ cal}^{0.5}/\text{cm}^{1.5}$.

More recently, JP9136985 and EP761291 issued to JUNG et al. disclose polymeric
5 dopes for the production of integrally skinned asymmetric membranes by the dry-wet
phase inversion method. The polymer dope comprises of a polymeric material of
polysulfone, polyethersulfone, polyimide, polyetherimide or a mixture of the polymers; a
mixed solvent of a main solvent such as N-methyl pyrrolidone, dimethylformamide,
dimethyl acetamide or dimethylsulfoxide and a co-solvent such as THF, dioxane,
10 methylene chloride, (m)ethyl-or propyl-acetate, chloroform; and an additive of formic acid
or ethanol.

There is still the need to prepare hollow fiber membranes having an ultrathin-skin
separating layer and the desired substructure morphology. The present invention has met
this need as a result of extensive studies wherein the key factors which determine the
15 properties of membranes were elucidated.

SUMMARY OF THE INVENTION

This invention relates to the preparation of ultra-thin skinned hollow fiber
membranes for gas separation. An objective of the present invention is to provide a simple
and economic process for manufacturing these ultra-thin skinned asymmetric hollow fiber
20 membranes.

Another aspect of the invention relates to the preparation of polymer dopes, the
polymer dopes and the method of using the polymer dopes in the synthesis of high
performance separation ultra-thin skinned asymmetric hollow fiber membranes. The
polymer dopes comprise a polymer in a moderate concentration and viscosity, a solvent,
25 and a suitable nonsolvent as an additive. A unique feature of this invention is the addition
of a suitable nonsolvent-additive (NSA) to the polymer dope in an amount appropriate for
bringing the polymer dope close to the incipient phase separation.

An effective NSA must have good miscibility and excellent diffusivity with the

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coagulant. The coagulant used must be a strong nonsolvent for a given polymer and easily miscible with the solvent and the NSA in the polymer dope. Water and aqueous solutions of small molecular organics are suitable to be used as nonsolvent-additives. These small molecular organic compounds must have low viscosity and excellent miscibility with water.

The present invention provides for the formulation of a polymer dope and a process for forming asymmetric hollow fiber membranes which exhibit high permeability and selectivity. The polymer dope contains a polymer as a membrane-former, a solvent and a nonsolvent-additive. Ideally, the polymer dope has a moderate polymer concentration, a moderate viscosity and is close to the incipient phase separation.

It is a feature of the present invention that the viscosity and state of the polymer dopes can be adjusted by the introduction of a suitable nonsolvent-additive into the polymer dope.

One aspect of the present invention provides for the preparation of polymer dopes for use in preparing ultrathin-skinned asymmetric hollow fiber gas separation membranes comprising: mixing a polymer and a mixture of a solvent and a non-solvent additive in relative amounts appropriate to bring the polymer dope close to the incipient phase separation wherein the polymer dope has a moderate polymer concentration and viscosity.

Another aspect of the present invention provides for a method of manufacturing high separation performance polymeric hollow fiber membranes for separating gases from each other, comprising of following steps: (a) mixing a polymer, a solvent, and a non-solvent-additive to form a polymer dope; (b) spinning the polymer dope by a Loeb-Sourirajan dry/wet phase inversion method (as described in US 3,133,132); (c) coagulating the internal and external surfaces to form a hollow fiber membrane; and (d) coating the hollow fiber membrane with a highly permeable material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the hollow fiber spinning apparatus;

FIG. 2 is a representation of a ternary phase diagram;

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FIG. 3 shows oxygen pressure-normalised flux and oxygen/nitrogen selectivity as a function of temperature for the hollow fiber membrane prepared in this invention;

FIG. 4 is a scanning electronic micrograph of cross-section of the membrane spun using water as the internal coagulant from the 28wt% polymer dope containing N-methyl-
5 2-pyrrolidone/water;

FIG. 5 is a scanning electronic micrograph of cross-section of the membrane spun from 28wt% polymer dope containing N-methyl-2-pyrrolidone/water, and using 50wt% ethanol/water as the internal coagulant.

DETAILED DESCRIPTION OF THE INVENTION

10 One aspect of this invention comprises a novel method for producing ultrathin-skinned asymmetric polysulfone hollow fiber membranes which exhibit high permselectivities for commercially important gas pairs. Additionally, the invention is directed to the ultrathin-skinned asymmetric hollow fiber membranes. The preparation of the hollow fiber membranes initially involves the formation of polymer dopes.

15 The present invention also includes polymer dopes, a method of using the polymer dopes for the preparation of high performance separation asymmetric hollow fiber membranes, and a process for the preparation of the polymer dopes comprising: mixing a polymer and a mixture of a solvent and an NSA in relative amounts appropriate to bring the polymer dope close to the incipient phase separation wherein the polymer dope has a
20 moderate polymer concentration and viscosity.

The mixture of the solvent and the NSA, in the appropriate mass ratio, is capable of dissolving a suitable concentration of polymer and being rapidly desolvated during the coagulation step. The solvent to NSA mass ratio varies, but in a preferred embodiment falls within the range of 2.6:1 to 19.3:1.

25 Solvents useful in the present invention include, but are not limited to, N,N-disubstituted amides, such as N-methyl-2-pyrrolidone, DMAc, DMF, and mixtures thereof. In a preferred embodiment of the invention, the solvent is a single component. Its concentration ranges from 50 wt% to 70 wt% depending on the amount of NSA used.

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The miscibility between the NSA and the coagulant (water) can be indicated by their solubility parameter difference ($\Delta\delta$) which was calculated using the following eqn.

(1) (Barton, handbook of Solubility Parameters and Other Cohesive Parameters, C.R.C. Press, Inc., Florida, (1983)):

$$\Delta\delta = [(\delta_{d,c} - \delta_{d,n})^2 + (\delta_{p,c} - \delta_{p,n})^2 + (\delta_{h,c} - \delta_{h,n})^2]^{0.5} \quad (1)$$

where subscript d, p, and h are dispersion, dipole and hydrogen-bonding components, and c and n represent coagulant and nonsolvent-additive, respectively. A smaller $\Delta\delta$ means a better miscibility. Suitable NSAs must have low viscosity and small molecular weight in order to have good diffusivity. Their molecular weights must be less than 100, preferably less than 60, and their viscosities less than 5 cp, preferable less than 3 cp at 25°C.

NSAs useful in the present invention include, but are not limited to, water, C₁-C₃ aliphatic alcohols or a mixture of one of the C₁-C₃ aliphatic alcohols and water. As shown in Table 1, these NSAs have a small solubility parameter difference with water ($\Delta\delta$), low viscosity and small molecular weight, particularly water. In a preferred embodiment of the invention, the aliphatic alcohol is a monoalcohol and the NSA is a single component. As a NSA, the concentration of water in the polymer dope is in the range from 3-5 wt% whereas for C₁-C₃ aliphatic alcohols, the level ranges from 15 to 25 wt%.

TABLE 1

Molecular Weight, viscosity of several small organic compounds
and their solubility parameter difference with water.

Compounds	Molecular Weight	Viscosity ^a (cp), 25°C	$\Delta\delta$ (cal/cm ³) ^{0.5}
water	18	0.89	0
methanol	32	0.544	9.95
ethanol	46	1.074	11.7
1-propanol	60	1.945	13.0
2-propanol	60	2.038	13.56
1-butanol	74	2.54	13.9
1-pentanol	88	3.618	14.7

Polymers that can be used for preparation of the polymer dopes include, but are not limited to, polysulfone, polyethersulfone, polyetherimide, poly(styrenes), including styrene-containing copolymers such as acrylonitrilestyrene copolymers, styrene-butadiene

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copolymers and styrene-vinylbenzylhalide copolymers; polycarbonates; cellulosic
 polymers, such as cellulose acetate-butyrate, cellulose propionate, ethyl cellulose, methyl
 cellulose, nitrocellulose, etc.; polyamides and polyimides, including aryl polyamides and
 aryl polyimides; polyethers; poly(arylene oxides) such as poly(phenylene oxide) and
 5 poly(xylene oxide); poly(esteramide-diisocyanate); polyurethanes; polyesters (including
 polyarylates), such as poly(ethylene terephthalate), poly(alkyl methacrylates),
 poly(acrylates), poly(phenylene terephthalate), etc.; polysulfides; polymers from
 monomers having alpha-olefinic unsaturation other than mentioned above such as poly
 (ethylene), poly(propylene), poly(butene-1), poly(4-methyl pentene-1), polyvinyls, e.g.,
 10 poly(vinyl chloride), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinylidene
 fluoride), poly(vinyl alcohol), poly(vinyl esters) such as poly(vinyl acetate) and poly(vinyl
 propionate), poly(vinyl pyridines), poly(vinyl pyrrolidones), poly(vinyl ethers), poly(vinyl
 ketones), poly(vinyl aldehydes) such as poly(vinyl formal) and poly(vinyl butyral),
 poly(vinyl amides), poly(vinyl amines), poly(vinyl urethanes), poly(vinyl ureas),
 15 poly(vinyl phosphates), and poly(vinyl sulfates); polyallyls; poly(benzobenzimidazole);
 polyhydrazides; polyoxadiazoles; polytriazoles; poly(benzimidazole); polycarbodiimides;
 polyphosphazines; etc., and interpolymers, including block interpolymers containing
 repeating units from the above such as terpolymers of acrylonitrile-vinyl bromide-sodium
 salt of para-sulfophenylmethallyl ethers; and grafts and blends containing any of the
 20 foregoing. Typical substituents providing substituted polymers include halogens such as
 fluorine, chlorine and bromine; hydroxyl groups; lower alkyl groups; lower alkoxy groups;
 monocyclic aryl; lower acyl groups and the like. In a preferred embodiment, the polymer
 is polysulfone. The polymer concentration is preferably in the range of about 15wt% to
 about 40wt%, more preferably between 20wt% to 35 wt%.

25 The method of manufacturing high separation performance polymeric hollow fiber
 membranes of the invention, comprises the following steps: (a) mixing a polymer, solvent,
 and an NSA to form a polymer dope; (b) spinning the polymer dope by the Loeb-
 Sourirajan dry/wet phase inversion method (as described in US 3,133,132); (c) coagulating
 and washing to form a hollow fiber membrane; and (d) coating the hollow fiber membrane
 30 with a highly permeable material.

In accordance with the present invention, the hollow fiber membranes are prepared
 using a phase inversion process. The nascent hollow fiber is formed by forcing the polymer

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dope through a tube-in-orifice spinneret while injecting an internal coagulant into the fiber lumen. After passing through an air-gap of a predetermined length, the nascent fiber is immersed into a coagulation bath. The coagulant acts as a nonsolvent, i.e., the coagulant does not dissolve the polymer to an appreciable extent. However, the coagulant is not to be confused with the NSA of the present invention. The temperature of the coagulation bath can be varied from 0°C to 100°C. Preferably, the coagulation bath temperature is in the range of 5°C to 50°C. Most preferably, the coagulation bath is maintained at room temperature.

During coagulation, the counter diffusion of the molecules of solvent and the coagulant cause phase separation to occur at both the internal and the external surfaces of the hollow fiber initially and the coagulation fronts move inward towards the center of the fiber wall. The passage through an air gap coupled with the immersion in the coagulation bath results in a very thin and dense outer skin layer.

The hollow fiber is then transferred from the coagulation bath to a washing bath. The solvents and/or NSA's remaining on the fiber after leaving the coagulation bath, are mostly washed away in the washing bath; however, if necessary, the fiber may be further washed by using a water spray and/or continued immersion in a water bath for a period of several hours up to a week.

The fibers are generally dried prior to application of the coating and assembly in an apparatus for gas separations. The drying may be conducted at about 0° to 100°C, conveniently about room temperature, e.g., about 15° to 35°C, and at about 5 to 95, preferably about 40 to 60, percent relative humidity.

The dried hollow fibers are then coated with a highly permeable material. The resultant coated hollow fibers display high gas permeability and selectivity. Gases such as, but not limited to, H₂, N₂, CH₄, He, CO₂, Ar, hydrogen sulfide, nitrous oxide, ammonia, O₂, and a hydrocarbon of 1 to about 5 carbon atoms, especially methane, ethane, and propane, can be effectively separated from gas mixtures using the hollow fiber membrane of the present invention.

Highly permeable materials are applied as a coating to the dried hollow fibers in order to seal the pores on the fiber surface. Without such a coating, the fiber will not have

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the desired selectivity.

Highly permeable materials useful in coating the dried hollow fibers may often have an average thickness ranging from about 0.0001 to 50 microns. In some instances, the average thickness of the coating is less than about 1 micron, and may even be less than about 5000 angstroms. The coating may comprise one layer or at least two separate layers which may or may not be of the same materials.

The coating may be applied in any suitable manner, e.g., by a coating operation such as spraying, brushing, immersion in an essentially liquid substance comprising the material of the coating or the like.

The materials for the coating may be natural or synthetic substances, and are often polymers, and advantageously exhibit the appropriate properties to provide occluding contact with the porous separation membrane. Synthetic substances include both addition and condensation polymers. Typical of the useful materials which can comprise the coating are polymers which can be substituted or unsubstituted, and which are solid or liquid under gas separation conditions, and include synthetic rubbers; natural rubbers; relatively high molecular weight and/or high boiling liquids; organic prepolymers; poly(siloxanes) (silicone polymers); polysilazanes; polyurethanes; poly(epichlorhydrin); polyamines; polyimines; polyamides; acrylonitrile-containing copolymers such as poly(α -chloroacrylonitrile) copolymers; polyesters (including polylactams and polyarylates), e.g., poly(alkyl acrylates) and poly(alkyl methacrylates) wherein the alkyl groups have, say, 1 to about 8 carbons, polysebacates, polysuccinates, and alkyd resins; terpinoid resins; linseed oil; cellulosic polymers; polysulfones, especially aliphatic-containing polysulfones; poly(alkylene glycols) such as poly(ethylene glycol), poly(propylene glycol), etc.; poly(alkylene) polysulfates; polypyrrolidones; polymers from monomers having α -olefinic unsaturation such as poly(olefins), e.g., poly(ethylene), poly(propylene), poly(butadiene), poly(2,3-dichlorobutadiene), poly(isoprene), poly(chloroprene), poly(styrene) including poly(styrene) copolymers, e.g., styrene-butadiene copolymer, polyvinyls such as poly(vinyl alcohols), poly(vinyl aldehydes) (e.g., poly(vinyl formal) and poly(vinyl butyral)), poly(vinyl ketones) (e.g., poly(methylvinylketone)), poly(vinyl esters) (e.g., poly(vinyl benzoate)), poly(vinyl halides) (e.g., poly(vinyl bromide)), poly(vinylidene halides), poly(vinylidene carbonate),

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poly(N-vinylmaleimide), etc., poly(1,5-cyclooctadiene), poly(methylisopropenylketone), fluorinated ethylene copolymer; poly(arylene oxides), e.g., poly(xylylene oxide); polycarbonates; polyphosphates, e.g., poly(ethylene-methylphosphate); and the like, and any interpolymers including block interpolymers containing repeating units from the above, and grafts and blends containing any of the foregoing. The polymers may or may not be polymerized after application to the porous separation membrane.

Particularly useful materials for coatings comprise poly(siloxanes). Typical poly(siloxanes) can comprise aliphatic or aromatic moieties and often have repeating units containing 1 to about 20 carbon atoms. The molecular weight of the poly(siloxanes) may vary widely, but is generally at least about 1000. Often, the poly(siloxanes) have a molecular weight of about 1,000 to 300,000 when applied to the porous separation membrane. Common aliphatic and aromatic poly(siloxanes) include the poly(monosubstituted and disubstituted siloxanes), e.g., wherein the substituents are lower aliphatic, for instance, lower alkyl, including cycloalkyl, especially methyl, ethyl, and propyl, lower alkoxy; aryl including mono or bicyclic aryl including bis phenylene, naphthalene, etc.; lower mono and bicyclic aryloxy; acyl including lower aliphatic and lower aromatic acyl; and the like. The aliphatic and aromatic substituents may be substituted, e.g., with halogens, e.g., fluorine, chlorine and bromine, hydroxyl groups, lower alkyl groups, lower alkoxy groups, lower acyl groups and the like. The poly(siloxane) may be cross-linked in the presence of a cross-linking agent to provide a silicone rubber, and the poly(siloxane) may be a copolymer with a cross-linkable comonomer such as .alpha.-methylstyrene to assist in the cross-linking. Typical catalysts to promote cross-linking include the organic and inorganic peroxides. The cross-linking may be prior to application of the poly(siloxane) to the porous separation membrane, but preferably the poly(siloxane) is cross-linked after being applied to the porous separation membrane. Frequently, the poly(siloxane) has a molecular weight of about 1,000 to 100,000 prior to cross-linking. Particularly advantageous poly(siloxanes) comprise poly(dimethylsiloxane), poly(phenylmethylsiloxane), poly(trifluoropropylmethylsiloxane), copolymer of .alpha.-methylstyrene and dimethylsiloxane, and post-cured poly(dimethylsiloxane)-containing silicone rubber having a molecular weight of about 1,000 to 50,000 prior to cross-linking. Some poly(siloxanes) do not sufficiently wet a polysulfone porous separation membrane to provide as much occluding contact as is desired. However, dissolving or dispersing the poly(siloxane) in a solvent which does not

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substantially affect the polysulfone can facilitate obtaining occluding contact. Suitable solvents include normally liquid alkanes, e.g., pentane, cyclohexane, etc.; aliphatic alcohols, e.g., methanol; some halogenated alkanes; and dialkyl ethers; and the like; and mixtures thereof.

5 The preferred coating material is silicone rubber (Sylgard-184, Dow Corning). The preferred method of applying the coating material consists of dissolving the coating material in a suitable solvent, than immersing the dried hollow fiber in the solution, followed by stripping the solvent by vacuum. Concentrations of coating solutions can vary from 1wt% to 10wt%, preferably 1wt% to 5wt%.

10 The hollow fibers of this invention may be spun using a spinning apparatus shown schematically in Figure 1. The polymer dope is prepared by combining a preformulated amount of the polymer, solvent and NSA in the mixing tank 2. The polymer dope is stirred with the mechanical stirrer 1. After the polymer is completely dissolved, the homogeneous polymer dope is then transferred into the solution tank 3. The dope is degassed and then
15 passed through filter 4 under nitrogen pressure wherein any undissolved particles are removed from the solution. The internal coagulant is contained in the internal coagulant tank 6. During the membrane spinning process, the filtered polymer dope and the internal coagulant are introduced separately through the spinneret 8 forming the nascent hollow fiber structure at ambient conditions, preferably 25+1°C and RH = 60-65%. The spinneret
20 is a tube-in-orifice type, a diagram of which is shown in the insert of Figure 1. The polymer dope is fed into the orifice of the spinneret and its flow rate is controlled by the gear pump 5. The internal coagulant is introduced under nitrogen pressure into the inner tube of the spinneret and its flow rate is controlled by the mass flow controller 7 to between 1 to 3 ml/min. The extrusion rate of the fiber is controlled. Tap water at room
25 temperature is used as the external coagulant in the coagulation bath 9, whereas tap water or a mixture of water and C₁-C₃ aliphatic alcohols is used as the internal coagulant. Different spinning conditions are employed depending on the specific polymer dope used. The spinneret is arranged such that the nascent fiber is extruded vertically downwards into the coagulation bath. The temperature of the bath is kept at 5-50 °C, preferably 5-30 °C.
30 The nascent fiber emerging from the tip of the spinneret passes through an air gap of predetermined length before entering the coagulation bath 9. After coagulation, the fibers are immersed in a washing bath 10, and then coiled into a storage tank 12. The path of the

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fiber is directed by the motor guide 11. The motor guide does not forcibly draw the fiber from the washing bath 10, per se. In other words, the take-up velocity of the hollow fiber is nearly the same as its free falling velocity in the coagulation bath. The hollow fiber is then kept in a storage tank for two days to stabilize the structure.

5 The membranes fabricated are commercially attractive regarding their separation performance, mechanical strength, fabrication method and other properties. This process is an economically viable process allowing for the production of reliable hollow fibers in large quantities owing to the fact that membrane materials having good selectivity as well as thermal and mechanical stability are commercially available, and the nonsolvent-
10 additives and the coagulants are inexpensive and have very little toxicity.

The hollow fibers of the present invention have very thin and dense outer skin layers supported by an interconnected microporous sublayer having very little resistance to gas flow. The outer skin layer, which is just beneath the silicone coating layer, is too thin to be measured by scanning electronic microscopy, so it must be estimated from gas
15 permeability measurements. For a silicone-coated asymmetric membrane, the pressure-normalized flux (P/L) through the membrane can be estimated by the Equation (2) given by Henis et al., (*J. Membrane Sci.*, Vol. 8, p. 233, (1981)):

$$\left(\frac{P}{L} \right) = \left(\frac{L_1}{P_1} + \frac{L_2}{P_2 + P_1 \varepsilon} \right)^{-1} \quad (2)$$

where L_1 is the apparent skin layer thickness of the asymmetric membrane; L_2 is the
20 thickness of the silicone-coating layer; P_1 is the gas permeability coefficient in asymmetric membrane; P_2 is the permeability coefficient of the coating silicone rubber layer; ε is the surface porosity. If the selectivity of the coated membrane is essentially equal to that of the asymmetric membrane measured at the same temperature and pressure difference, the resistance of the silicone-coated layer to gas permeation is negligible due to its high gas
25 permeability coefficient, very small surface porosity of asymmetric membrane and thin coating layer thickness. Under such conditions, the apparent skin layer thickness (L_1) of asymmetric membranes may be determined by the following equation:

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$$L_1 = \frac{P_1}{\left(\frac{P}{L}\right)} \quad (3)$$

It was reported that the permeability coefficient of O₂ through polysulfone material is 1.06 X 10⁻¹⁰ cm³·cm/cm²·cmHg·sec and the O₂/N₂ selectivity is 6.2 at 25°C (Pinnau et al., *J. Appl. Polym. Sci.*, Vol. 43, p. 1491, (1991)). (P/L) is the gas pressure-normalized flux, (cm³(STP)/cm²·cmHg·sec). Thus, the apparent effective skin thickness for a silicon coated asymmetric membrane of the invention, ranges from 350Å to 700Å as estimated from gas permeability measurements and reported permeability coefficient data of dense films formed from the same polymers. Clearly, the final product is a composition having a complex morphology comprising an outer and inner skin layer where in between lies a highly open porous support which is easily seen by scanning electron microscopy as shown in Figures 4 and 5.

Overall, the entire porous separation membrane is sufficiently thick so that no special apparatus is required for its handling. Frequently, the porous separation membrane has a thickness of about 20 to 500, preferably, about 50 to 200, most preferably 300 microns. When the multicomponent membrane is in the configuration of a hollow fiber, the fiber may often have an outside diameter of about 200 to 1000, preferably about 200 to 800 microns and wall thicknesses of about 50 to 300, preferably 200 microns.

The polymers of the present invention are highly selective aromatic polymers, preferably, polysulfone. Polysulfone is a very important gas separation membrane material. It has good selectivity for separating oxygen from nitrogen and separating helium, hydrogen and carbon dioxide from nitrogen and methane (Kesting et al. *Polymeric Gas Separation Membranes*, John Wiley & Sons, INC, (1993), Haraya et al., *J. Membrane Sci.*, 71(1992)13). Polysulfones have good thermal resistance (high glass transition temperature) and mechanical stability, and are generally easy to prepare as asymmetric membranes by the Loeb-Sourirajan phase inversion method.

In a preferred embodiment of the invention, polymer dopes are prepared having polymer concentrations of 25wt%-32wt% and absolute viscosities of 10,000-60,000cp at 25°C. Polysulfone is dissolved in the mixture of N-methyl-2-pyrrolidone (NMP) and an

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NSA. The mass ratio of NMP:NSA varies depending on the nature of the NSA. The NSAs of the present invention include water, C₁-C₃ alcohols and mixtures of one of the alcohols and water. Hollow fibers were spun by the dry/wet method using water and/or the mixture of alcohol/water as the internal coagulant and water as the outer coagulant. The schematic diagram of the hollow fiber spinning apparatus is shown in Fig. 1.

The following theory is presented as a guide for the skilled artisan and should not be interpreted as limiting the scope or essence of the claimed invention.

The asymmetric membrane is formed using a phase inversion process of a polymer solution in the presence of a coagulant. The ternary phase diagram (Figs. 2A and 2B), consisting of a polymer (A), coagulant (B) and a solvent (C), is herein used to explain asymmetric membrane formation. The key features of the diagram are the stable single phase region (I), the unstable liquid-liquid two-phase region (II), the gelation region (III), and the Metastable region (IV). Region (I) represents a single phase, wherein the polymer is completely dissolved in the solvent or the solvent mixture. This is a stable homogeneous solution. Region (II) represents a relatively high concentration of coagulant and/or NSA. The excess nonsolvent for the polymer in the solution results in liquid-liquid phase separation. Region (III) represents a relatively high concentration of polymer (A). Here the polymer is not soluble in the minimal quantities of solvent, so the polymer forms a gel. Region (IV) represents metastable composition. In this region, the solution undergoes phase separation by a nucleation and growth mechanism. At or close to the spinodal curve, the mechanism of phase separation may change to the so called "spinodal decomposition" in which periodic and network structures may form without nucleation. Z represents the critical point wherein at lower polymer concentrations the separation between the single phase region (I) and the biphasic region (II) depends upon the ratio of solvent to coagulant and/or NSA. For macromolecules, the polymer concentration at the critical point is extremely low. Therefore, the critical point (Z) of a polymer composition is typically much closer to the (B)-(C) axis than in lower molecular weight compositions.

Incipient phase separation occurs when the local concentration of the solvent becomes so small that region (I) disappears. In general, the shape and size of a single-phase region (I) depends on the nature of the polymer, the solvent/additive and the coagulant, polymer concentration and the temperature. Upon the addition of a nonsolvent-

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additive (NSA) into a polymer solution, region (IV) and region (II) shift toward the (A)-(B) axis as represented by comparing Fig. 2A to Fig. 2B. As a result, the single phase region (I) becomes smaller. Upon the addition of an excess of NSA, the line represented by X-Z reaches the polymer-solvent axis and region (I) disappears completely, i.e., no single phase exists. This is the point where incipient phase separation occurs.

The polymer dopes of the present invention consist of a polymer, solvent and an NSA. While maintaining a moderate concentration of polymer, the relative ratio of the solvent and NSA are controlled so as to minimize the area of region (I), and yet confine the overall composition to region (I). The resultant polymer dope is maintained near the incipient phase separation. By maintaining the polymer dope near the incipient phase separation, the phase separation process is accelerated and the amount of coagulant required is reduced.

The closer the X-Z curve is to the (A)-(B) axis, the closer the solution is to the point of incipient phase separation, and the faster phase inversion will tend to occur upon the addition of the coagulant. As mentioned above, the introduction of the coagulant to the polymer/solvent solution causes a counter diffusion of the molecules of solvent and the coagulant resulting in phase separation occurring at both the internal and the external surfaces of the hollow fiber initially and the coagulation fronts moving inward towards the center of the fiber wall. The enhanced rate of coagulation restricts the available time in which the polymer molecules can approach equilibrium by undergoing further packing and/or conformational rearrangements. Thus, membranes with a thin skin layer would be obtained. However, the actual phase separation kinetics and final membrane structure will depend on the miscibility and diffusion rate of the NSA-coagulant and the solvent-coagulant systems.

The type of phase separation depends on: i) the exchange rate of the solvent-coagulant; ii) the outflow rate of the NSA; and iii) the ratio of rates of the solvent to the NSA outflow. Rapid outflow of the solvent and NSA from the outer region routinely tends to cause phase separation to move directly into the gelation region (phase I $\rightarrow$ III in Fig. 2). As a result, thin and dense skin layer tends to form. This is favourable for making gas separation membrane.

When efflux of the NSA is more rapid than that of the solvent, the rapid loss of the

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NSA increases the polymer/solvent interaction, and the polymer/solvent interaction controls the local structure. In this case, if the solvent and the NSA have strong affinity for the coagulant, than rapid gelation may still occur resulting in the formation of membrane with a thin and dense skin layer. However, if the solvent has poor affinity with the coagulant, the rapid outflow of the NSA coupled with the slow exchange of the solvent and coagulant result in a delayed gelation. Thus, a dense thick skin layer is then formed.

On the contrary, if the efflux of solvent is more rapid than that of the NSA, the rapid efflux of solvent tilts the local balance toward liquid-liquid phase separation. Liquid-liquid phase separation easily occurs prior to gelation because the polymer concentration does not increase fast enough. The resulting membrane is likely to have a porous skin layer which is not suitable for gas separation.

Prior to the addition of the coagulant, the polymer dopes are maintained close to the incipient phase separation. The extent of closeness to the incipient phase separation can be determined by the coagulation value, which has been defined as the quantity of a coagulant in grams required to make 2g of a polymer in a 100 g polymer solution turbid, i.e., the lower the coagulation value of the polymer dope - the closer the polymer dope is to the incipient phase separation. (Kesting et al., U.S. Patent 4,871,494; Wang et al., J. Membrane Sci., Vol. 98, (1995) 233).

The formulation of the polymer dope composition is based on Eqn.(4) which relates the mass ratio of nonsolvent-additive to solvent ($R_{a/s}$) and its coagulation value (G_v) (Wang et al. J. Membrane Sci., vol. 98, (1995) 233). This equation is expressed in terms of the precipitation values of the nonsolvent-additive and the coagulant in the binary polymer-solvent system (Wang et al., J. Appl. Polym. Sci., vol. 50,(1993)1693).

$$R_{a/s} = \frac{\frac{98}{100} PV_a - \frac{PV_a}{PV_c} G_v}{98 + \frac{PV_a}{PV_c} G_v} \quad (4)$$

In Eqn.(4), PV_a is the precipitation value of nonsolvent-additive (a); PV_c is the precipitation value of coagulant (c); $R_{a/s}$ is the mass ratio of nonsolvent-additive to solvent in the polymer dope and G_v is the coagulation value.

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With increasing polymer concentration, the X-Z curve is shifted slightly closer to the polymer-solvent axis (A)-(B) due to the stronger interaction between the polymer and the solvent mixture (Wijmans et al., *Polymer*, Vol. 26, p. 1539, (1985)). The influence of temperature on the phase separation region depends on the interactions of polymer-solvent-nonsolvent additive. For polysulfone/solvent/water or the C₁-C₃ alcohol systems, the single phase region will increase with increasing temperature. (Wang et al., *J. Appl. Polym. Sci.*, Vol. 50, p. 1693, (1993)).

The final structure of the fiber membrane is determined by the interactions of the polymer-solvent-NSA system in the solution and phase separation caused by the counter diffusion of solvent/NSA and coagulant. The introduction of a sufficient amount of the NSA enhances the formation of large polymer aggregates and minimizes the dissolving effect of the solvent for the polymer, especially at relatively high polymer concentrations. In this case, the polymer chains have a smaller excluded volume because of a more tightly coiled conformation. Thus, an initially homogeneous polymer solution becomes microscopically heterogeneous.

As region (I) disappears, the polymer dope has local concentrations in the metastable region (IV). When liquid-liquid phase separation occurs in the metastable region, the polymer molecules agglomerate forming a polymer-rich phase; and the nucleation growth in the polymer-lean phase result in the formation of close cells. The final membrane morphology is still controlled by phase separation kinetics determined by the exchange rates of the solvent and the NSA with the coagulant during the immersion coagulation process. If a solvent and a NSA have strong affinity for a coagulant, quick exchange of these components restricts the nucleation growth in the polymer-lean phase, and the spinodal decomposition may quickly take place in the two-phase region. This accelerated phase separation process restricts further agglomeration of polymer aggregates and the membrane formed has small macrovoids or sponge-like structures. The rapid solidification process also prevents the coalescence of the spinodal decomposition polymer matrix; thus, the substructure has good interconnectivity between macrovoids.

However, if the coagulant has a strong affinity with the solvent but poor affinity with the NSA, the rapid loss of solvent leads to a strong nonsolvent environment that intensifies nucleation growth and results in the formation of superaggregates and the

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resultant membranes have big macrovoids.

A unique aspect of this invention is the choice of a suitable nonsolvent-additive in producing hollow fiber membranes by the dry/wet phase inversion process. The skin layer thickness is inversely proportional to the coagulation kinetics of the nascent membrane with the coagulant. The nonsolvent-additive plays a dominant role in accelerating phase inversion kinetics. In selecting a nonsolvent-additive, it is of primary importance to select one with excellent mutual affinity to both the solvent and coagulant. In preparing asymmetric membranes by the immersing phase inversion method, water is the most preferred coagulant. The non-solvent-additive selected should be readily miscible with water. Therefore, water, C₁-C₃ aliphatic alcohols and mixtures of one of the alcohols and water are good candidates in the selection of nonsolvent- additives.

The desired concentration of a nonsolvent-additive in the polymer dope depends on the nature of polymer, solvent and nonsolvent-additive as well as temperature. Nonsolvents are categorized as strong nonsolvents and weak nonsolvents in terms of Hansen solubility parameter difference ($\delta_{\text{nonsolvent}} - \delta_{\text{polymer}}$). A strong nonsolvent is defined as one having a $\Delta\delta > 6\text{cal}^{0.5}/\text{cm}^{1.5}$. A weak nonsolvent is defined as one with a $\Delta\delta < 6\text{cal}^{0.5}/\text{cm}^{1.5}$ (Kesting et.al, U. S. Patent, 4,871,494). It has been demonstrated that it was not reliable to determine the non-solvent-additive concentration in the polymer dope based on the solubility parameter, whereas the precipitation value of the nonsolvent in a particular polymer/solvent system is more precise in the determination of the concentration of the nonsolvent-additive in the polymer dope (Wang et al., J. Appl. Polym. Sci., vol. 50, (1993) 1693). A nonsolvent-additive with a higher precipitation value can be introduced at a higher concentration in the polymer dope. According to Eqn.(4), the maximum possible mass ratio of nonsolvent-additive to solvent ($(R_{a/s})_{\text{max}}$) is obtained when the coagulation value is zero. The mass ratio of nonsolvent-additive to solvent in the range of 0 to $(R_{a/s})_{\text{max}}$ may be required to achieve the desirable composition for a given coagulation value. The optimal composition is to have the polymer dope close to the phase separation point; therefore, the coagulation value should be very small.

A feature of this invention is the design and formulation of a polymer dope with a suitable coagulation value by the addition of a nonsolvent-additive for making the desired hollow fibers having improved permeability and selectivity. This allows the coagulation

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process to occur at an extremely rapid rate and prevent formation of large unsealable surface pores and thick skin layer. The choice of the coagulation value is determined by the precipitation values of the nonsolvent-additive and coagulant and the interactions of polymer/solvent/nonsolvent-additive. Usually, the dissolving power of solvent system for a polymer reduces with increasing polymer concentration due to interactions between the polymer and the constituents of the solvent system. It is generally believed that coagulation values are different for different solvent systems depending on the interaction between the solvent system and polymer, which is concentration dependent. A higher coagulation value is expected for a system where the interaction strongly depends on the polymer concentration. The mass ratio of the nonsolvent-additive to solvent in the polymer dope can be determined using Eqn.(4) for a desired coagulation value. The desired mass ratio of nonsolvent-additive to solvent in the polymer dope is different for different nonsolvent-additives and solvents in terms of their precipitation values. Due to strong interaction between water and hydrophobic polymers, the coagulation values of 1-3g are required for the polysulfone/NMP/H₂O system when the polymer concentration is in the range of 25wt%-32wt%. The corresponding mass ratios of H₂O:NMP are in the range of 1:13.7 to 1:19.3 which is much lower than that of propionic acid:NMP used in U.S. Patent 4,871,494. Also, when ethanol was used as the nonsolvent-additive, the mass ratios of ethanol:NMP are in the range of 1:2.4 to 1:2.9.

The polymer concentration of the polymer dope must be sufficiently high to produce hollow fiber membranes having a dense surface separating layer and a good mechanical support layer for gas separation. A polymer concentration of about 20%-40% by weight, and preferably 20%-32% by weight, in the dope may be needed to achieve the resulting hollow fiber membranes having the desired selectivity and mechanical strength. Too high a polymer concentration tends to cause difficulty in dissolving the polymer, degassing the polymer dope, and spinning of hollow fiber membranes, whereas membranes produced from too low a polymer concentration have low selectivity and poor mechanical strength. In this invention, the optimal polymer concentrations are in the range of 25wt%-32wt% for polysulfone. Furthermore, the desired polymer concentration depends on the type of solvent and nonsolvent-additive used and the operating pressure of the resulting membranes.

Viscosity has a significant effect during the spinning of the hollow fiber membrane.

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The desired viscosity may be achieved by the selection of a suitable nonsolvent-additive which forms a hydrogen-bond complex with the solvent. The formation of this complex greatly increases the viscosity of the solvent system which in turn causes the viscosity of the polymer dope to increase dramatically. The absolute viscosity is preferably between 10,000-60,000 cp at 25°C. In this invention, the formation of the complex of water and N-methyl-2-pyrrolidone yields polymer dopes having a high viscosity.

The polymer dope temperature is typically held between about 0°C-100°C and is chosen so as to maintain the dope near the incipient phase separation point. High temperatures are less preferred when the nonsolvent-additive has a low boiling point. Preferably, the temperature is maintained between 15-50°C. The more preferred temperature is room temperature.

In the phase inversion process for membrane making, the exposure of the fiber to the air in the air-gap is very important for forming a thin dense outer layer. The effect of this drying process mainly depends on the rheology of the nascent fiber, the coalescence caused by the surface tension of the nascent membrane, and the volatility of the solvent and nonsolvent-additive. After spinning, the polymer molecules in the nascent fiber are rearranged. The coalescence and deformation of polymer aggregates induced by the surface tension also play an important role in forming a dense skin layer. This process is critical to the formation of an asymmetric hollow fiber membrane having a thin, dense outer layer from a polymer/solvent/nonsolvent-additive ternary solution system. On the other hand, the polymer concentration on the surface of the nascent membrane may increase due to the evaporation of the solvent and NSA. Alternatively, the absorption of moisture may result in phase separation, particularly in a polymer dope whose composition is close to the point of phase separation. The air-gap is generally kept about 1-50 cm, preferably about 1-20 cm. For different nonsolvents, the air-gaps are different. The air-gap should be optimized to produce the best asymmetric hollow fibers. The optimal gap will depend upon many factors, including: a) the interaction of polymer-internal coagulant; b) the boiling point of the solvent system; c) the rate of spinning; d) the wall thickness of hollow fibers; e) the internal coagulant; f) the temperature of dope; and g) the membrane making environment.

During the outer drying process, the internal coagulant is injected immediately after

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extrusion through a spinnerette. The internal coagulant seriously effects the highly open lumen formation and membrane structure. Suitable nonsolvent strength and good miscibility with the solvent are important for forming good hollow fiber membranes. The macrovoids in the substrate can be efficiently reduced by the use of an internal coagulant having a suitable strength for the polymer. In the process of this invention, water and the mixture of water/C₁-C₃ alcohol are preferred as the internal coagulants.

The kinetics of desolvation during the coagulation process is another important factor in producing asymmetric hollow fibers exhibiting high permeability and good mechanical strength. The skin layer thickness depends on how rapidly the coagulation of the membrane wall occurs due to the exchange of the solvent/non-solvent additive with the coagulant. One important factor that controls this phase separation kinetics is the coagulant tolerance of the polymer dope, that is, how close the polymer dope is near to the phase separation point. The closer the polymer dope is to the phase separation point, the faster the phase inversion tends to occur and the thinner the skin layer thickness will be. Another factor which controls the rates of desolvation during the wet coagulation process is the mutual miscibility between the solvent system and the coagulant. Many nonsolvents for a given polymer can be used as coagulant. Water is the most favorable one from an economic and environmental standpoint. Therefore, the solvent and nonsolvent-additive selected is preferably easily miscible in water. Ideally, when the nascent hollow fiber is immersed into a water bath, quick coagulation and fiber solidification occur over the membrane wall. Fast coagulation of the substrate results in spinodal decomposition and less coalescence between the polymer-rich phase and the polymer-lean phase. The substrate of the resulting hollow fiber exhibits good interconnection and low gas transport resistance.

EXPERIMENTAL DETAILS

The hollow fibers recorded in the examples below were prepared by the dry-wet spinning process. The schematic diagram of the spinning apparatus is shown in Figure 1. A mixture of the solvent and nonsolvent additive (NSA) was first prepared according to the mass ratio determined using equation (4) for a desirable coagulation value. The polymer was then added in the solvent mixture to give the polymer dope with a desirable polymer concentration. The polymer was dissolved in the solvent mixture with agitation.

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Viscosities of polymer dopes were measured using a Haake falling ball viscometer at 25°C. The homogeneous polymer dope was introduced into a solution tank. During the hollow fiber spinning process, the polymer dope was extruded through the orifice of a spinnerette while an internal coagulant was simultaneously injected into the tube of the spinnerette fiber lumen. The spinnerette is a single hole tube-in-orifice type. The temperature of the spinnerette was maintained at room temperature (24-26°C). The spinnerette was arranged such that the hollow fiber was extruded vertically downwards into the coagulation bath. The nascent fiber passed through an air-gap of a predetermined length before entering the water bath (25-30°C). The take-up velocity was 4-8m/min. The hollow fiber was washed with a spray of water for up to 3 days and then removed from the water bath and dried at room temperature. Each of the hollow fiber test cells consisted of twenty to thirty hollow fibers having a length of 20 to 30cm. The hollow fibers were coated with the solution containing 3wt% Sylgard-184 in n-pentane while applying a vacuum in the fiber lumen.

The hollow fiber test cells were placed in a pressure vessel. The permeation rates of pure helium, carbon dioxide, oxygen and nitrogen were measured at room temperature (25±1°C) using a soap flowmeter. The pressure difference across the hollow fiber was kept at 5 bar. The pressure-normalized flux $(P/L)_i$ was then determined. The ideal selectivity of gas "i" relative to nitrogen is the ratio of the pressure normalized flux of gas "i" to that of the nitrogen.

The following examples are for illustrative purposes only and are not intended to, and should not be construed to limit the scope of the claimed invention in any way.

EXAMPLE 1

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and water (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 16.1/1. The polymer concentration is 30wt%. The coagulation value and viscosity of the polymer dope are 2.2g and 54,430cp at 25°C, respectively. The hollow fibers with an outer diameter of about 750µm and an inner diameter of 425µm were prepared using water as the internal coagulant. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and nitrogen and their ideal selectivities relative to nitrogen were determined at 25±1°C and pressure

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difference of 5 bar. The results are given in Table 2. The apparent skin layer thickness, L_1 of the membrane is determined using Eq. 3.

TABLE 2

Sample	(P/L) _i , (GPU)				Ideal selectivity			L_1 (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
1	152.0	90.1	14.9	2.16	70.4	41.7	6.9	711
2	187.2	97.2	17.1	2.56	73.1	37.9	6.7	620

(P/L): pressure-normalized flux

5 $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2\text{-cmHg-s}$

EXAMPLE 2

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and water (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 16/1. The polymer concentration was 28wt%. This polymer dope had a coagulation value of 2g and viscosity of 38,100cp at 25°C. The hollow fibers were prepared using the spinnerette with an orifice diameter/inner diameter of the tube of 0.5/0.15mm. Hollow fibers with an outer diameter of about 550µm and an inner diameter of 300µm were prepared using water as the internal coagulant. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and nitrogen and their ideal selectivities relative to nitrogen were determined at 25±1°C and pressure difference of 5 bar. The results are given in Table 3. The apparent skin layer thickness, L_1 is determined using Equation 3.

TABLE 3

Sample	(P/L) _i , (GPU)				Ideal selectivity			L_1 (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
1	155.2	116.5	20.2	3.33	46.6	35.0	6.06	525
2	234.7	160.3	26.8	4.77	49.2	33.6	5.62	395
3	237.3	154.5	28.3	4.54	52.1	34.0	6.16	375

(P/L): pressure-normalized flux

20 $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2\text{-cmHg-s}$

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EXAMPLE 3

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and water (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 16/1. The polymer concentration is 28wt%. This polymer dope had a coagulation value of 2g and viscosity of 38,100cp at 25°C. Hollow fibers were prepared using the spinnerette with an orifice diameter/inner diameter of the tube of 0.5/0.15mm. The internal coagulant was 50wt% of 2-propanol and water. The resulting hollow fibers displayed an outer diameter of about 580μm and an inner diameter of 350μm. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and nitrogen and their ideal selectivities relative to nitrogen were determined at 25±1°C and pressure difference of 5 bar. The results are given in Table 4.

TABLE 4

Sample	(P/L) _i , (GPU)				Ideal selectivity			L ₁ (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
1	169.2	96.7	18.2	2.82	60.0	34.3	6.47	582
2	165.0	110.0	19.8	3.10	53.2	35.5	6.37	535
3	175.4	119.1	23.2	3.61	48.6	33.0	6.4	457

(P/L): pressure-normalized flux**1 GPU = 1×10⁻⁶ cm³(STP)/cm²-cmHg-s****EXAMPLE 4**

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and water (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 16/1. The polymer concentration is 28wt%. This polymer dope had a coagulation value of 2g and viscosity of 38100cp at 25°C. The hollow fibers were prepared using the spinnerette with an orifice diameter/inner diameter of the tube of 0.6/0.15mm. The internal coagulant was water. Hollow fibers with an outer diameter of about 610μm and an inner diameter of 350μm were prepared. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and

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nitrogen and their ideal selectivities relative to nitrogen were determined at $25\pm 1^\circ\text{C}$ and pressure difference of 5 bar. The results are given in Table 5.

TABLE 5

Sample	(P/L) _i , (GPU)				Ideal selectivity			L ₁ (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
1	154.0	92.0	17.5	3.07	50.1	30.0	5.69	606
2	241.0	161.0	31.2	5.18	46.5	31.1	6.03	340

(P/L): pressure-normalized flux

5 1 GPU = 1×10^{-6} cm³(STP)/cm²-cmHg-s

EXAMPLE 5

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and water (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 16/1. The polymer concentration is 28wt%. This polymer dope had a coagulation value of 2g and viscosity of 38,100cp at 25°C. The hollow fibers were prepared using the spinnerette with an orifice diameter/inner diameter of the tube of 0.6/0.15mm. The internal coagulant was a mixture of 50wt% water and 50wt% ethanol. The resulting hollow fibers have an outer diameter of about 620μm and an inner diameter of 370μm. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and nitrogen and their ideal selectivities relative to nitrogen were determined at $25\pm 1^\circ\text{C}$ and pressure difference of 5 bar. The results are given in Table 6.

TABLE 6

Sample	(P/L) _i , (GPU)				Ideal selectivity			L ₁ (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
1	205.0	113.5	23.0	3.29	62.3	34.5	6.98	461
2	201.6	134.5	31.1	6.20	46.5	31.1	5.03	341

(P/L): pressure-normalized flux

1 GPU = 1×10^{-6} cm³(STP)/cm²-cmHg-s

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EXAMPLE 6

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and water (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 16/1. The polymer concentration was 28wt%. This polymer dope had a coagulation value of 2g and viscosity of 38,100cp at 25°C. The hollow fibers were prepared at different coagulation bath temperatures. The spinnerette with an orifice diameter/inner diameter of the tube of 0.5/0.15mm was used. The internal coagulant was tap water at about 26°C. Hollow fibers with an outer diameter of about 550μm and an inner diameter of 325μm were prepared. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and nitrogen and their ideal selectivities relative to nitrogen were determined at 25±1°C and pressure difference of 5 bar. The results are given in Table 7.

TABLE 7

Temp (°C)	(P/L) _i (GPU)				Ideal selectivity			L ₁ (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
20-21	270.0	199.9	30.6	6.0	45.0	33.3	5.10	346
15-16	155.2	158.6	30.7	8.53	18.2	18.6	3.60	--
10-11	196.2	173.0	33.0	9.30	21.1	18.6	3.56	--

(P/L): pressure-normalized flux

1 GPU = 1×10^{-6} cm³(STP)/cm²-cmHg-s**EXAMPLE 7**

The polymer dope was prepared by dissolving polysulfone (P-1800, Amoco Performance) in a solvent mixture of N-methyl-2-pyrrolidone and ethanol (as a nonsolvent-additive) according to the mass ratio of solvent/nonsolvent-additive of 2.66/1. The polymer concentration was 28wt% and the polymer dope had a coagulation value of 1.5g and viscosity of 12,246cp at 25°C. The hollow fibers were prepared using the spinnerette with an orifice diameter/inner diameter of the tube of 0.5/0.15mm. The internal coagulant was water. The resulting hollow fibers have an outer diameter of about 650μm and an inner diameter of 320μm. The pressure-normalized fluxes of helium, carbon dioxide, oxygen and nitrogen and their ideal selectivities relative to nitrogen were

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determined at $25 \pm 1^\circ\text{C}$ and pressure difference of 5 bar. The results are given in Table 8.

TABLE 8

Sample	(P/L) _i (GPU)				Ideal selectivity			L ₁ (Å)
	He	CO ₂	O ₂	N ₂	He/N ₂	CO ₂ /N ₂	O ₂ /N ₂	
1	176.3	132.4	23.0	4.12	42.8	32.1	5.59	461
2	185.7	155.0	24.7	5.02	37.0	32.0	4.92	--
3	163.4	158.0	27.8	5.94	27.5	26.6	4.68	--
4	143.8	157.4	29.5	8.2	16.1	19.2	3.59	--
5	138.3	136.6	24.2	5.6	24.7	24.4	4.32	--

(P/L): pressure-normalized flux

1 GPU = 1×10^{-6} cm³(STP)/cm²-cmHg-s

- 5 An examination of Example 1 to Example 7 reveals that the polysulfone hollow fiber membranes prepared from NMP/H₂O solvent system with the mass ratio of 16:1 and NMP/ethanol solvent system with the mass ratio of 2.66/1 exhibit high permeability and selectivity. The results also show that coagulation bath temperature seriously affect the membrane permeability and selectivity. For the NMP/H₂O solvent system, the decrease in
- 10 coagulation bath temperature also decreases selectivity of the membranes. The oxygen pressure-normalized flux and the selectivity of oxygen with respect to nitrogen as a function of temperature of one of the samples are shown in Figure 3. Figures 4 and 5 depict the scanning electron micrographs of the hollow fibers spun using water and a mixture of 50wt% ethanol/water as the internal coagulant, respectively. Many regular
- 15 finger-like macrovoids appear on the cross-section of the hollow fibers spun using water as the internal coagulant, whereas the big macrovoids near the inner substrate are significantly reduced by the use of the mixtures of 50wt% ethanol/water as the internal coagulant.

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CLAIM

1 1. Formulation of polymer dopes, comprising:
2 mixing a polymer, a solvent and a non-solvent additive in relative amounts appropriate to
3 bring the polymer dope close to the incipient phase separation wherein the polymer dope
4 has a moderate polymer concentration and viscosity.

1 2. A polymer dope comprising a polymer, a solvent and a non-solvent additive
2 wherein the polymer dope is close to the incipient phase separation and has a moderate
3 polymer concentration and viscosity.

1 3. The polymer dope as set forth in claim 2, wherein the solvent is an N,N-
2 disubstituted amide.

1 4. The polymer dope as set forth in claim 2, wherein the nonsolvent-additive is
2 water, a C₁-C₃ aliphatic alcohol or a mixture of a C₁-C₃ aliphatic alcohol and water with
3 the proviso that the alcohol is not glycerol.

1 5. The polymer dope as set forth in claim 3, wherein the solvent is N-methyl-
2 2-pyrrolidone and the non-solvent additive is a C₁-C₃ aliphatic alcohol or a mixture of a
3 C₁-C₃ aliphatic alcohol and water with the proviso that the alcohol is not glycerol.

1 6. The polymer dope as set forth in claim 2, wherein the polymer
2 concentration is in the range of 20wt% to 32wt%.

1 7. The polymer dope as set forth in claim 2, wherein the polymer dope is close
2 to phase separation point and the coagulation value is between 1g to 3g for water.

1 8. The polymer dope as set forth in claim 2, wherein the polymer is
2 polysulfone.

1 9. The polymer dope as set forth in claim 5, wherein the mass ratio of N-

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2 methyl-2-pyrrolidone:water is in the range of 13.7:1 to 19.3:1.

1 10. The polymer dope as set forth in claim 5, wherein the mass ratio of N-
2 methyl-2-pyrrolidone:ethanol is in the range of 2.6:1 to 2.9:1.

1 11. The polymer dope of claim 2, wherein the concentration of the solvent
2 ranges from 50 wt% to 70 wt% based upon the weight of the dope.

1 12. The polymer dope as set forth in claim 6, wherein the polymer
2 concentration is in the range of 25 wt% to 32 wt %.

1 13. The polymer dope of claim 2, wherein the polymer dope has an absolute
2 viscosity in the range of 10,000-60,000cp at 25°C.

1 14. The polymer dope as set forth in claim 3, wherein the N,N-disubstituted
2 amide is N-methyl-2-pyrrolidone, dimethylacetamide or DMF.

1 15. A method of manufacturing high separation performance polymeric hollow
2 fiber membranes for separating gases from each other, comprising of following steps :

3 (a) mixing a polymer, a solvent, and a non-solvent-additive to form a
4 polymer dope;

5 (b) spinning the polymer dope by the Loeb-Sourirajan dry/wet phase
6 inversion method;

7 (c) coagulating and washing to form a hollow fiber membrane; and

8 (d) coating the hollow fiber membrane with a highly permeable
9 material.

1 16. The method according to claim 15, wherein the polymer is polysulfone.

1 17. The method according to claim 15, wherein the nonsolvent-additive is
2 water, a C₁-C₃ aliphatic alcohol or a mixture of one of the alcohols and water with the
3 proviso that the alcohol is not glycerol.

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1 18. The method according to claim 15, wherein the solvent is an N,N-
2 disubstituted amide.

1 19. The method according to claim 15, wherein an external coagulant is tap
2 water.

1 20. The method according to claim 15, wherein an internal coagulant is tap
2 water, or a mixture of water and one of the C₁-C₃ aliphatic alcohols.

1 21. The method according to claim 15, wherein the spinning step is performed
2 with a spinnerette.

1 22. The method according to claim 15, wherein the spun fiber prepared in step
2 (b) passes through an air gap ranging from 1 cm to 25 cm at ambient conditions.

1 23. The method according to claim 22, wherein the ambient conditions are at
2 temperature of 24-26°C and relative humidity of 60%-65%.

1 24. The method according to claim 19, wherein the temperature of the external
2 coagulant is in the range from 5°C to 50°C.

1 25. The method according to claim 15, wherein the hollow fibers of step (c) are
2 desolvated and washed in tap water at room temperature.

1 26. The method according to claim 15, wherein the hollow fiber membrane
2 prepared in step (c) is dried under ambient conditions.

1 27. The method according to claim 15, wherein the coating step (d) is
2 performed using a coating solution containing 1-5wt% silicone rubber and n-pentane under
3 vacuum.

1 28. The method according to claim 18, wherein the N,N-disubstituted amide is

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2 N-methyl-2-pyrrolidone or dimethylacetamide.

1 29. The method according to claim 15, wherein the temperature of the polymer
2 dope during spinning is in the range from 15 to 50 °C.

1 30. The method according to claim 20, wherein the temperature of the internal
2 coagulant during spinning is in the range of 24 to 26 °C.

1 31. The method according to claim 29, wherein the temperature of the polymer
2 dope during spinning is in the range of from 20 to 30°C.

1 32. The method according to claim 15, wherein the polymer dope of step (a) is
2 essentially homogenous.

1 33. The method according to claim 17, wherein the NSA is either water or a
2 mixture of water and a C₁-C₃ alcohol and the water is in a range of 3 to 5 wt% and the C₁-
3 C₃ alcohol is in a range of 15 to 25 wt% based upon the weight of the dope.

1 34. A membrane for separating and/or purifying gases, comprising polysulfone
2 wherein the membrane is prepared by the method of claim 15.

1 35. The membrane as set forth in claim 34, wherein the apparent skin layer
2 thickness is between 300 to 700Å.

1 36. The membrane as set forth in claim 35, wherein the gases are He, CO₂, O₂,
2 N₂ and CH₄.