Structures and Gas Separation Properties of Asymmetric Polysulfone Membranes Made by Dry, Wet, and Dry/Wet Phase Inversion

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SYNOPSIS

Integrally skinned asymmetric gas separation membranes were prepared by (i) dry, (ii) wet, and (iii) dry/wet phase inversion processes. The membranes were cast from a polysulfone/methylene chloride/1,1,2-trichloroethane/2-methyl-2-butanol casting system. Wet and dry/wet phase inversion membranes were quenched in methanol. Membranes made by dry/wet phase inversion using convective evaporation showed optimum gas separation performance. The average O_2/N_2 and He/N_2 selectivities of these membranes were within 85% of those determined for a dense, solution-cast polysulfone film, suggesting that the ultrathin skin layers were essentially defect free. The average apparent skin layer thickness of all samples tested was 270 Å. Scanning electron photomicrographs revealed that optimum membranes made by dry/wet phase inversion consist of an ultrathin skin layer, a tightly packed nodular transition layer, and an open-cell, sponge-like substructure. Dry/wet phase inversion membranes prepared by free-standing evaporation resulted either in high flux and low selectivity membranes or essentially defect-free membranes with fluxes lower than those made by convective evaporation. Dry-phase inversion membranes exhibited extremely low gas fluxes due to thick (17.5 μm) skin layers. On the other hand, wet phase inversion membranes showed O_2/N_2 selectivities < 1, indicating that gas transport was determined by pore flow through skin layer defects.

INTRODUCTION

The search for a process to produce perfect integrally skinned asymmetric membranes for gas separation was initiated soon after the pioneering work of Loeb and Sourirajan indicated the possibility of generating a cellulose acetate membrane consisting of an ultrathin, essentially dense skin layer supported by an open-celled substructure.[1] Gas permeation properties of asymmetric membranes are predominantly determined by the thickness and microscopic structure of the skin layer. Optimum membrane properties are obtained if the skin layer is defect free and its thickness is minimized. A defect-free skin layer guarantees that gas transport is determined by a solution/diffusion mechanism.[2] If the skin layer is defect free and the substructure resistance to gas transport negligible, the selectivity of an asymmetric membrane will be equal to the intrinsic selectivity of the membrane material.[3,4]

The formation of asymmetric membranes is the result of microphase separation phenomena that occur during an evaporation step and/or quench step of an initially thermodynamically stable polymer solution.[5] Consequently, distinctions can be drawn regarding the conditions under which the microphase separation process occurs to generate the final membrane morphology, as schematically illustrated in Figure 1 and discussed below.
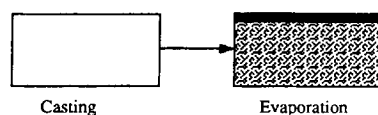
Flat-sheet integrally skinned asymmetric membranes are generally made by casting a solution consisting of polymer, solvents, and additives onto a suitable substrate. If the nonsolvent components are less volatile than the solvent components, evaporation will ultimately produce a critical nonsolvent concentration that causes the cast membrane to be

1. Dry Phase Inversion

Casting   Evaporation

2. Wet Phase Inversion

Casting   Quench
              Evaporation

3. Dry/Wet Phase Inversion

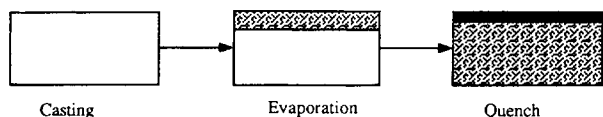Casting   Evaporation   Quench
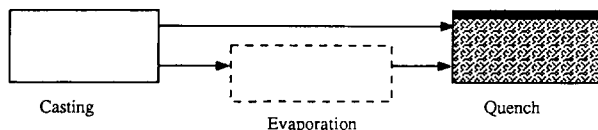
Figure 1 Schematic representation of phase inversion processes.

transformed from a single-phase to a two-phase structure. If the solvent and nonsolvent components are removed solely by evaporation, membrane formation is defined as a *dry phase inversion process*.[6]

Alternatively, phase instability and structure formation can also be achieved by immersion of a cast membrane in a quench medium that is a nonsolvent for the membrane-forming polymer. If the *entire* phase separation process is the result of solvent/nonsolvent exchange during the quench step, the structure formation process is often referred to as a *wet phase inversion process*.[6] The wet phase inversion process is the most common approach to prepare asymmetric membranes for microfiltration,[7] ultrafiltration,[8] reverse osmosis,[9] and gas separation.[10,11] Most ultrathin (skin layer thickness < 2,000 Å) asymmetric gas separation membranes made by wet phase inversion show skin layer pores (defects) that lead to a substantial decrease in selectivity.[12] Posttreatments of various types can be used to render defective asymmetric membranes suitable for gas separation.[10,13–16] However, these treatments add complexity to the membrane production process.

Membrane structures can also be formed by a microphase separation process in which the outermost region of the cast membrane undergoes phase separation induced by solvent evaporation, while the bulk of the structure is formed by solvent/nonsol-

vent exchange during a quench step. This type of structure formation is defined as a *dry/wet phase inversion process*.[17]

Only a few studies on gas separation membranes made by dry/wet phase inversion have been reported in the literature.[17–19] Interfacial dry phase inversion of these membranes was induced by *free-standing evaporation* of solvent components. Organic nonsolvents (methanol, acetone, etc.) have preferably been used as quench media for the wet phase inversion step.[18,19] Integrally skinned asymmetric membranes made by dry/wet phase inversion can show extremely thin skin layers (< 1,000 Å). The utility of these membranes for gas separations was limited due to skin layer defects; therefore, various posttreatments have been developed to render dry/wet phase inversion membranes suitable for gas separation.[20]

This article presents the gas separation properties of asymmetric polysulfone membranes made by dry, wet, and dry/wet phase inversion processes. It will be demonstrated that optimized dry/wet phase inversion processes can generate simultaneously ultrathin and essentially defect-free integrally skinned asymmetric membranes.

EXPERIMENTAL

Materials and Membranes

Polysulfone, Udel P 1700, was kindly supplied by Amoco, Ridgefield, CT. Polysulfone is an amorphous, hydrophobic polymer with a glass transition temperature of 185°C.

Dense Film Preparation

A 5 wt % solution of polysulfone in chloroform was poured into a stainless steel ring supported by a glass plate. Solvent was evaporated from the film for 24 h at 25°C. Thereafter, the clear film was removed from the glass plate and dried in a vacuum oven for 3 d by slowly raising the temperature from 25–190°C. Finally, the temperature was held constant at 190°C for 24 h. A DSC run on a dry film sample showed no evidence of residual solvent left in the dried film.

Asymmetric Membrane Preparation

The selection of solvents, nonsolvents, and quench medium for membrane preparation was based on casting solution formulations employed in the formation of integrally skinned asymmetric polyethersulfone membranes.[17] Membranes were made from 12.2 wt % polysulfone, 52.8 wt % methylene chloride,

20.3 wt % 1,1,2-trichloroethane, and 14.7 wt % 2-methyl-2-butanol. The casting solution was chosen to be close to the thermodynamic instability limit, i.e., binodal composition, to assure that interfacial phase separation could be induced on reasonable time scales by solvent evaporation. Methanol was used as quench medium.

Dry Phase Inversion Membranes

Polysulfone membranes were cast on glass plates with a knife gap of 250 μm. The cast membranes were air-dried at 25°C for 48 h and postdried in a vacuum oven at 100°C for 5 d.

Wet Phase Inversion Membranes

Polysulfone membranes were cast on glass plates at 25°C with a knife gap of 250 μm. Immediately after casting, the membranes were quenched in methanol at 25°C, washed for 12 h, air-dried for 24 h, and finally postdried in a vacuum oven at 100°C for 6 h.

Dry/Wet Phase Inversion Membranes: Free-standing Evaporation

Polysulfone membranes were made as discussed above. However, the cast membranes were exposed to air for 10–90 sec prior to quenching in methanol. The initially clear, nascent membranes became slightly turbid after ~ 15 sec, indicating the onset of phase separation.

Dry/Wet Phase Inversion Membranes: Forced Convective Evaporation

Polysulfone membranes were prepared as discussed above. A gas stream (air 100% RH) was blown across the membrane surface from a $\frac{1}{4}''$ tube for a period of 10 sec. Interfacial phase separation in the cast membrane occurred immediately at the onset of the blowing process, as indicated by appreciable turbidity in the nascent membranes. Careful removal of the topmost layer of such structures indicated a clear, stable solution phase below a thin layer of interfacially phase separated material. After an additional free-standing evaporation step of 15 sec, the membranes were quenched in methanol and dried under the conditions discussed above.

Gas Permeation Experiments

Dense Films

The permeabilities of helium, nitrogen, and oxygen for a solution-cast polysulfone film were measured at 25°C and an upstream pressure of 3.5 atm. The permeation data were taken using the standard permeation techniques employed in our labs.[21] A downstream pressure of 10 mm Hg or less was always negligible relative to the upstream pressure.

Asymmetric Membranes

Pure gas pressure-normalized fluxes reported in this study were obtained at 25°C for membrane samples of 12.6 cm^2 surface area at a pressure difference of 3.5 atm. Volumetric gas flow rates were determined with soap bubble flowmeters. The ideal selectivity of a membrane, $\alpha_{A,B}$, is defined as the pure gas pressure-normalized flux ratio of gas A and gas B

$$\alpha_{A,B} = \frac{(P/L)_A}{(P/L)_B}. \tag{1}$$

If the selectivity of an asymmetric membrane is essentially equal to that of the membrane material measured at the same temperature and pressure difference, an apparent skin layer thickness can be calculated by

$$L = P_i/(P/L)_i, \tag{2}$$

where P_i is the permeability coefficient of gas i, as determined on thick isotropic films of known thickness.

RESULTS AND DISCUSSION

The pure gas permeation properties of integrally skinned asymmetric polysulfone membranes made by the dry/wet phase inversion technique using *convective evaporation* are shown in Figures 2 and 3. The average O_2/N_2 and He/N_2 selectivities of 40 randomly selected membrane samples were 5.3 and 56, respectively. The average selectivities of the asymmetric membrane samples were within 85% of the intrinsic O_2/N_2 and He/N_2 selectivities of polysulfone, as determined for a solution-cast, dense film of known thickness (Table I). These results indicate that the transport properties of the asymmetric membranes were predominantly determined by a solution/diffusion mechanism. Hence, the skin layers can be considered essentially defect free. Apparent skin layer thicknesses were determined based on the oxygen permeability coefficient of polysulfone (Table I) using eq. (2). The average apparent skin layer thickness of all integrally skinned polysulfone membrane samples tested was 270 Å. Apparent skin
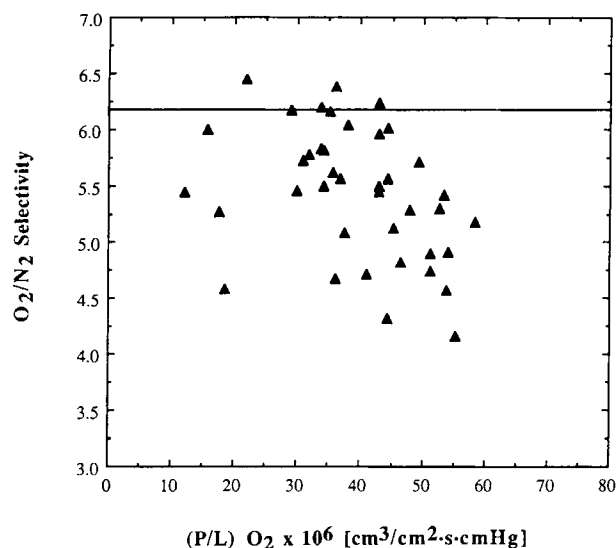
Figure 2 O_2/N_2 selectivities and pressure-normalized oxygen fluxes of asymmetric polysulfone membranes made by dry/wet phase inversion using convective evaporation. $T = 25°C$; $\Delta p = 3.5$ atm.

layer thicknesses of individual membrane samples ranged between 180–900 Å, as shown in Figure 4.

It should be noted that the calculated, *apparent skin layer thickness* is only an approximation of the *actual skin layer thickness*. If the selectivities of asymmetric membranes are different from those of the membrane material, it is expected that the mo-
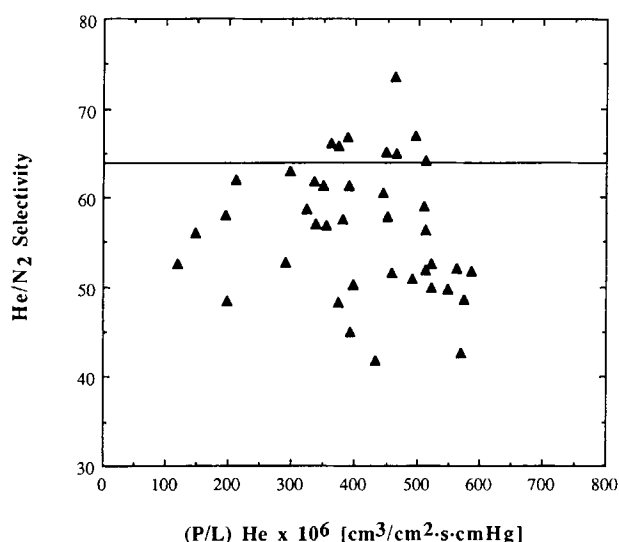

Figure 3 He/N_2 selectivities and pressure-normalized helium fluxes of asymmetric polysulfone membranes made by dry/wet phase inversion using convective evaporation. $T = 25°C$; $\Delta p = 3.5$ atm.

Table I   Permeability Coefficients and Ideal Selectivities of a Solution/Cast Polysulfone Film at 25°C and 3.5 atm Upstream Pressure

Permeability Coefficient [Barrers][a]			Selectivity	
N_2	O_2	He	O_2/N_2	He/N_2
0.171	1.06	10.84	6.2	63

[a] Barrer = 10^{-10} [cm^3(STP) cm/cm^2 s cmHg].

lecular skin layer structure differs somewhat from that of the bulk membrane material.

Lower selectivities of asymmetric membranes can be the result of pores (defects) or enhanced free volume in the ultrathin skin layers. Skin layer pores are defined here as passageways that allow communication between the upstream and downstream side of the membrane by a *Knudsen* or *viscous flow* process. Even pores on the order of 5–10 Å over an area fraction as small as 10^{-5} degrade the selectivity of membranes unacceptably.[12] On the other hand, enhanced free volume in the ultrathin skin layers is equivalent to a decrease of inter- and intramolecular polymer chain packing density. However, the gas transport through such a skin layer with enhanced free volume compared to that of the bulk material is still determined by a solution/diffusion mechanism. This increase in free volume results in higher *effective* permeability coefficients in the skin layers.[22] Hence, the *actual* skin layer thickness of asymmetric membranes having higher free volume is expected to be larger than the *apparent* skin layer thickness based on the permeability coefficient of the bulk material. It has been noted that the skin layer structure of asymmetric polysulfone hollow fiber membranes made from Lewis acid:base solvent complexes can show higher free volume compared to that of the bulk material.[22-24] Evidence for increased free volume in the skin layers of such membranes was provided by DSC and sub-T_g annealing experiments. It was shown that sub-T_g annealing at 110°C after 166 h resulted in a 30% decrease in gas fluxes compared to unannealed membranes samples as a consequence of free volume reduction.[23]

On the other hand, studies of integrally skinned polyestercarbonate membranes made by a similar process to that described here showed higher selectivities compared to those obtained for the bulk material. In this case, it has been hypothesized that possible orientation-induced increases in segmental

packing density in the skin layers, i.e., decrease of free volume, resulted in an increase in selectivity.[25] It is expected, therefore, that the actual skin thickness of membranes having lower free volume is smaller than the apparent skin thickness based on the permeability coefficient of the bulk material.

The above discussion suggests that the apparent skin layer thicknesses of asymmetric polysulfone membranes reported in the present work might also differ somewhat from the actual skin layer thicknesses. Sub-T_g annealing experiments on membranes of this study at 110°C showed a decrease in gas fluxes between 30–40%, similar to those seen in polysulfone hollow fibers as discussed above. It can be expected, therefore, that the apparent skin layer thicknesses reported here are 30–40% lower than the actual skin layer thicknesses.

It has been hypothesized that *all* asymmetric membranes contain some skin layer defects due to incomplete coalescence of polymer in the skin layer.[26,27] Therefore, it is expected that the selectivities of asymmetric membranes will be lower compared to those obtained for dense films. Contrary to this hypothesis, several asymmetric membrane samples with skin layer thicknesses as thin as 200 Å (Fig. 4) exhibited O_2/N_2 and He/N_2 selectivities equal to or *even higher* than those determined for a dense polysulfone film. This result indicates the possibility of producing simultaneously ultrathin and defect-free asymmetric polysulfone membranes by a dry/wet phase inversion technique using forced convective convective evaporation.
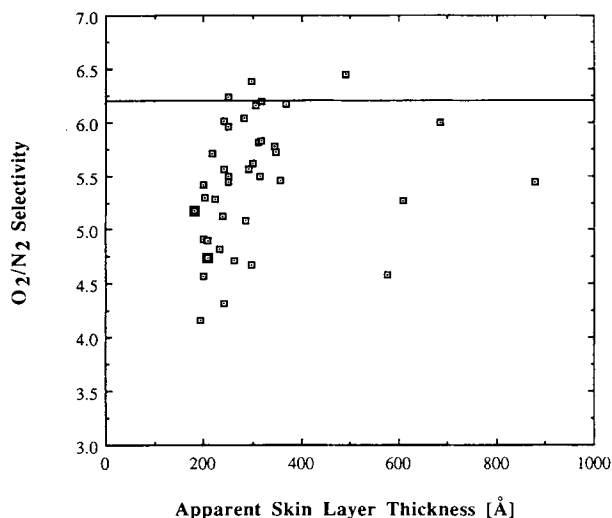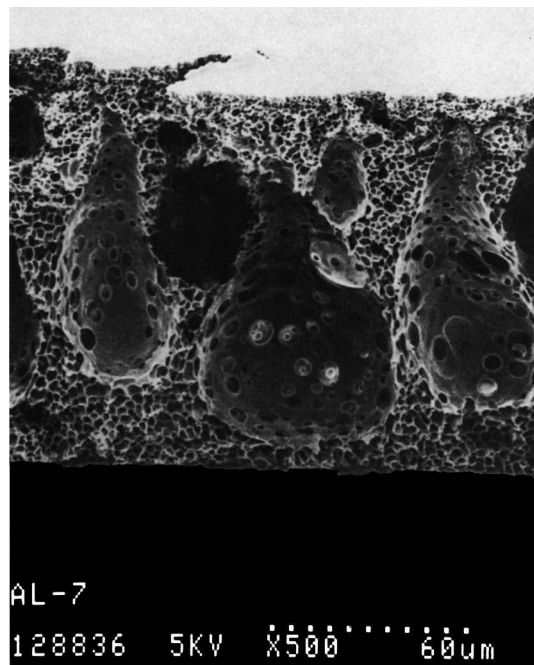

Figure 5 Cross-section of an asymmetric polysulfone membrane made by dry/wet phase inversion using convective evaporation. Magnification 500X.

The structural features of asymmetric polysulfone membranes made by dry/wet phase inversion using forced convective evaporation have been elucidated from scanning electron microscopy (SEM) studies. The asymmetric membrane sample used for SEM analysis showed an O_2/N_2 selectivity of 6.0 and an apparent skin layer thickness of 250 Å, as determined by permeation measurements using eq. (2). The cross-section of the asymmetric polysulfone membrane sample consists of a sponge-like structure that contains large macrovoids, as shown in Figure 5. Since the skin layer of the membrane sample was essentially defect free, it is suggested that macrovoid formation for membranes made by dry/wet phase inversion is not necessarily due to intrusion of the quench medium by stress-induced rupture of the skin layer, as proposed for macrovoids in ultrafiltration membranes.[28] Figure 6 shows the outermost region of the asymmetric polysulfone membrane sample at a magnification of 100,000. The top structure consists of polymer aggregates, often referred to as nodules.[29] Individual nodules appear to be approximately 200–400 Å in diameter. The overall thickness of the top layer is about 4,000 Å; however, the top layer consists of two distinctly different regions, i.e., an ultrathin, dense skin layer supported by rather porous transition layer. It is interesting
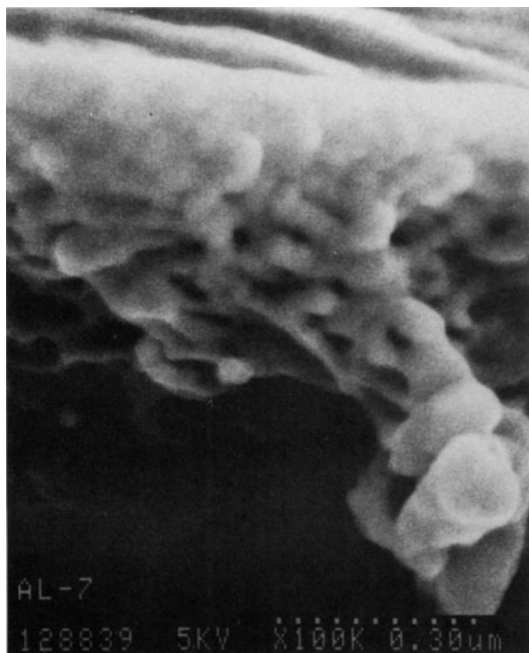

Figure 4 O_2/N_2 selectivities vs. apparent skin layer thicknesses of polysulfone membranes made by dry/wet phase inversion.

Figure 6 Top structure of an asymmetric polysulfone membrane made by dry/wet phase inversion using convective evaporation. Magnification 100,000×.

to note that the average nodule size is approximately equal to the apparent skin layer thickness. Therefore, it appears that the actual skin layer could be the result of complete fusion of surface nodules occurring during the membrane formation process.

To investigate which physical processes determine the ultimate structure and permeation prop-

erties of asymmetric polysulfone membranes made by dry/wet phase inversion using forced convective evaporation, further studies were carried out on membranes formed by (i) dry, (ii) wet, and (iii) dry/wet phase inversion using free-standing evaporation, respectively.

The cross-section of a polysulfone membrane made by dry phase inversion, i.e., complete evaporation of solvents and additives without a quench step, is shown in Figure 7. In this case, the membrane consists of very thick, dense skin layer ($\sim$ 17.5 μm) supported by a coarse, sponge-like, macrovoid-free substructure. The gas permeation rates through this membrane were so low that an accurate measurement could not be carried out with the constant pressure-variable volume method employed for asymmetric membrane characterization. The results obtained for dry phase inversion membranes demonstrate clearly that a quench step is of utmost importance to obtain ultrathin-skinned asymmetric membranes using the casting formulation employed in this study.

Polysulfone membranes made by wet phase inversion showed on the average (10 samples) a pressure-normalized oxygen flux of 6×10^{-4} cm^3/cm^2 s cmHg and an O_2/N_2 selectivity of 0.91, indicating that gas transport was predominantly determined by pore flow. These results demonstrate that the skin layers of membranes made by wet phase inversion were highly defective. The cross-section of a membrane sample, as shown in Figure 8, consists of a sponge-like substructure containing two types
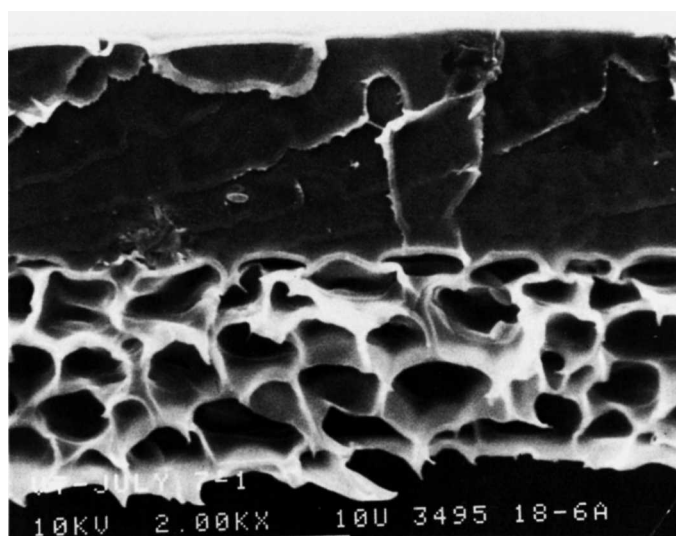

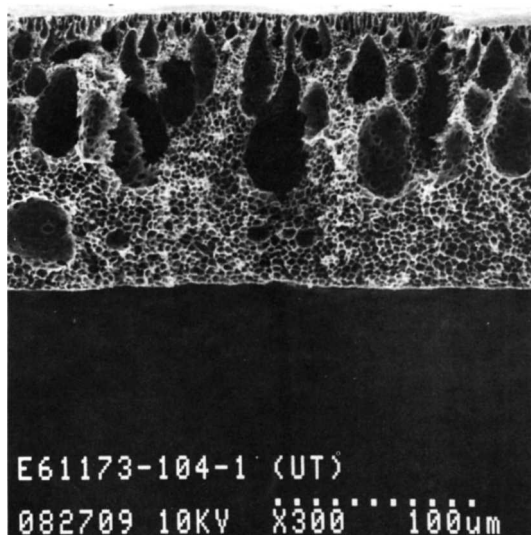**Figure 7** Cross-section of an asymmetric polysulfone membrane made by dry phase inversion. Magnification 2,000×.

Figure 8 Cross-section of an asymmetric polysulfone membrane made by wet phase inversion. Magnification 300×.

of macrovoids. Large macrovoids are present in the bulk structure, similar to those seen in membranes made by dry/wet phase inversion using forced convective evaporation (Fig. 5), with smaller macrovoids occurring directly underneath the membrane

surface. Since the skin layers of membranes made by wet phase inversion were highly defective, a likely mechanism for the formation of the small macrovoids is stress-induced rupture of the skin layer by intrusion of the quench medium as suggested by Strathmann and Kock.[28] The outermost region of wet phase inversion membranes shown in Figure 9 consists of a bicontinuous, highly porous network. A nodular structure, present in dry/wet phase inversion membranes made by convective evaporation, is not apparent. At even higher magnification, the outermost region appears to be a highly imperfect structure, as shown in Figure 10. A distinct, high-integrity skin layer cannot be discerned from the photomicrograph. It should also be noted that membranes made by wet phase inversion showed a dull surface possibly due to surface roughness and differences in refractive indices between polymer matrix and surface pores.

The structural features of membranes made by the dry and the wet phase inversion, respectively, indicate that the unique structure of the outermost region of membranes made by dry/wet phase inversion using forced convective evaporation must be the combined result of microphase separation processes occurring during the evaporation and quench steps.
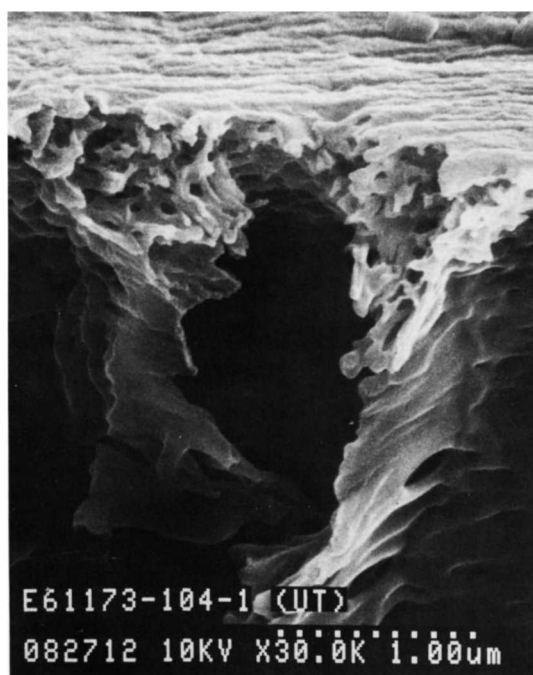

Figure 9 Top structure of an asymmetric polysulfone membrane made by wet phase inversion. Magnification 30,000×.

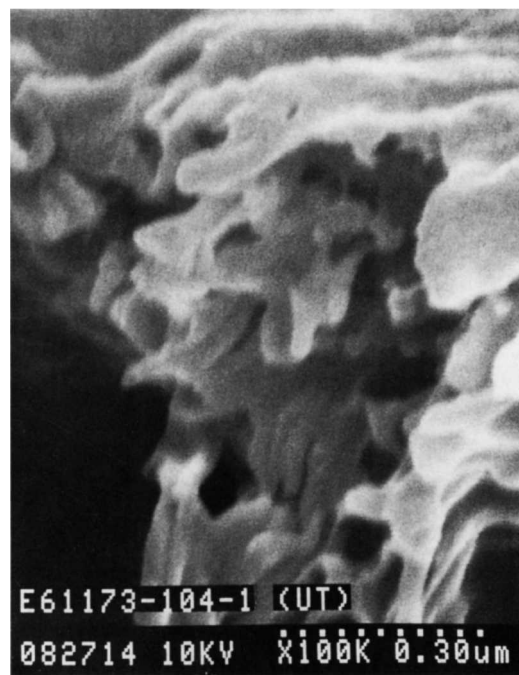**Figure 10** Top structure of an asymmetric polysulfone membrane made by wet phase inversion. Magnification 100,000×.

To investigate the influence of evaporation kinetics on membrane structure and gas permeation properties, a series of polysulfone membranes were made by dry/wet phase inversion using free-standing evaporation. The kinetics of phase separation occurring during the evaporation step were investigated by light transmission experiments, as recently proposed by Reuvers.[30] The light transmission device used in the present study is shown in Figure 11. After casting, solvent evaporation-induced phase separation was observed in the membranes as indicated by optical inhomogeneities, which caused the light transmittance to decrease with time. A relative light transmission (RLT) is defined as:

$$RLT = 1 - \frac{LT_{max} - LT}{LT_{max} - LT_{min}}, \qquad (3)$$

where LT_{max} is the maximum light transmission through a membrane at time t_0 as sensed by the photodetector, LT is the light transmission at time t, and LT_{min} is the minimum light transmission at infinite time. The relationship between free-standing evaporation time and relative light transmission for polysulfone membranes cast from the formulation of the present study is shown in Figure 12(a). The onset of interfacial phase separation in the nascent membranes occurred 15 sec after casting. Thereafter, the relative light transmittance decreased rapidly and remained essentially constant at a low level for evaporation times longer than 60 sec.

The permeation properties of membranes made by dry/wet phase inversion using free-standing evaporation are shown in Figures 12(b) and 12(c).
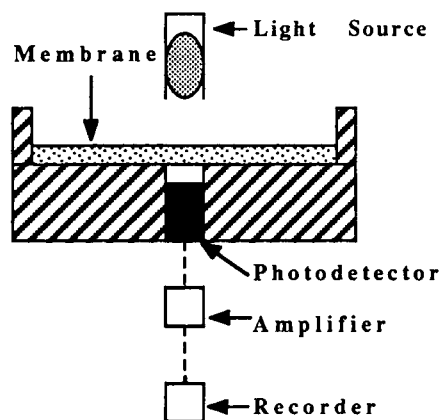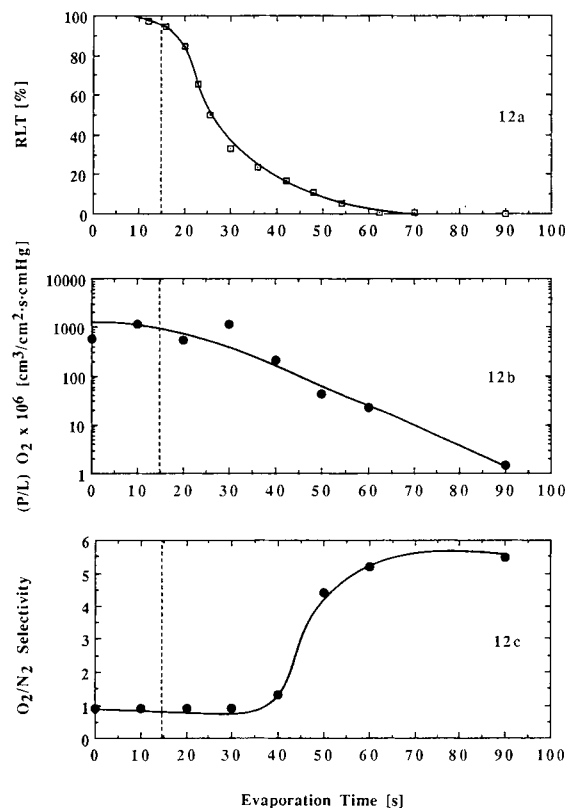
Figure 12 Evaporation time vs. (a) relative light transmission (RLT), (b) pressure-normalized O_2 fluxes, and (c) O_2/N_2 selectivity of polysulfone membranes made by dry/wet phase inversion using free-standing evaporation.

Each data point represents the average of six randomly selected membrane samples. It must be noted that membranes quenched after 0–15 sec free standing evaporation time showed only a negligible decrease of relative light transmittance until immersed in the methanol, indicating that phase separation was not induced during the evaporation step. Hence, these membranes can be classified as wet phase inversion membranes. All membranes made by wet phase inversion showed O_2/N_2 selectivities of < 1 combined with pressure-normalized O_2-fluxes between $6–12 \times 10^{-4}$ cm^3/cm^2 s cmHg, indicating that gas transport was predominantly determined by pore flow through skin layer defects.

The relative light transmittance decreased markedly between 15–40 sec evaporation time, indicating the occurrence of phase separation in the membranes [Fig. 12(a)]. Therefore, membranes quenched after evaporation times longer than 15 sec are classified as dry/wet phase inversion membranes. The resulting membranes are still highly
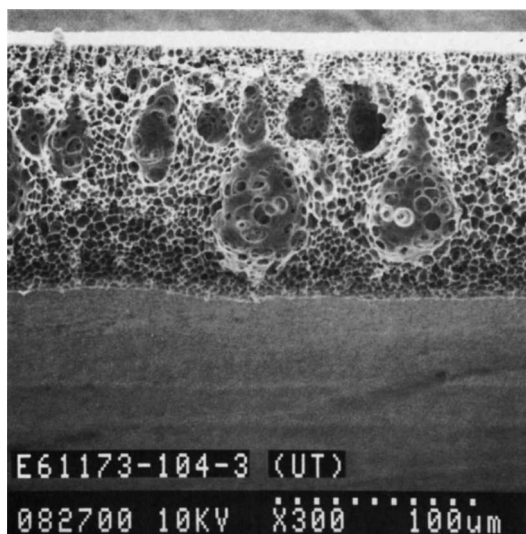
Figure 11 Experimental set-up for light transmission experiments.

Figure 13 Cross-section of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 30 sec. Magnification 300×.

defective, as indicated by O_2/N_2 selectivities of < 1. Figure 13 shows the cross-section of a membrane quenched after 30 sec free-standing evaporation. It is interesting to note that the sponge-like, macro-void-containing structure appears to be very similar to that of membranes made by dry/wet phase in-

version using convective evaporation (Fig. 5). The outermost region shows a distinct, very thin skin layer supported by a bicontinuous, highly porous network, as shown in Figures 14 and 15. It appears that the structure of the visually glossy skin layer is the result of the microphase separation processes that occur during the evaporation step, compared to the dull, highly imperfect structure seen in wet phase inversion membranes (Fig. 10). However, since the O_2/N_2 selectivity of dry/wet phase inversion membranes quenched 30 sec after free-standing evaporation was < 1, it can be concluded that the fusion of surface nodules was incomplete.

Membranes quenched after an evaporation period of 40 sec or more showed a substantial increase in O_2/N_2 selectivity combined with a dramatic decrease in pressure-normalized oxygen fluxes. Membranes quenched after an evaporation period of 60 sec showed optimum performance. It is interesting to note that during this optimum period the relative light transmittance approached zero. The average O_2/N_2 selectivity of these membranes was 5.2 combined with an average pressure-normalized oxygen flux of $2.2 \times 10^{-5} \text{cm}^3/\text{cm}^2$ s cmHg. The apparent skin layer thickness of these membranes was 490 Å. Dry/wet phase inversion membranes made by forced convective evaporation showed, on the average, essentially the same O_2/N_2 selectivity; however, the
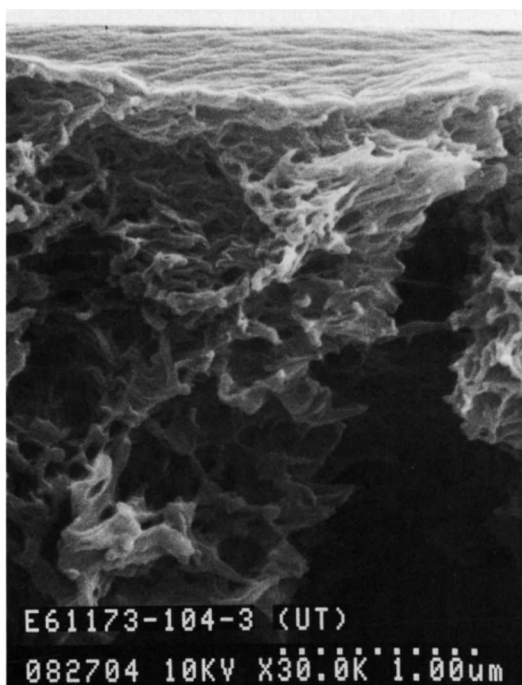

Figure 14 Top structure of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 30 sec. Magnification 30,000×.
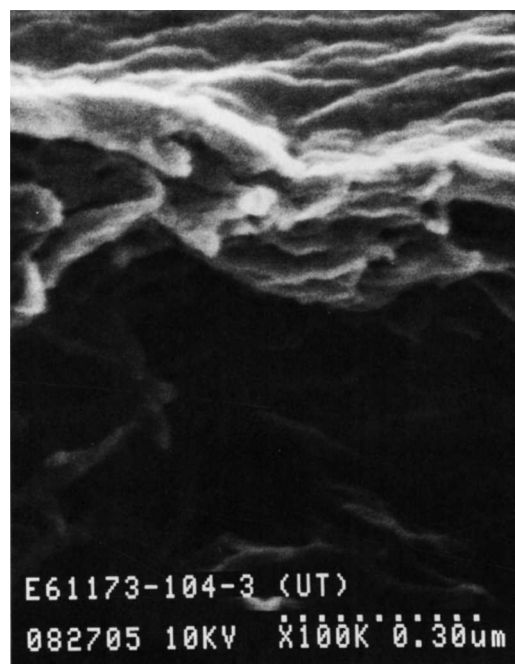

Figure 15 Top structure of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 30 sec. Magnification 100,000×.

pressure-normalized oxygen flux was about 1.8 times higher compared to that of membranes made by dry/wet phase inversion using free-standing evaporation. Again, the cross-sections of these membranes appeared very similar to those seen for membranes made by dry/wet phase inversion using convective evaporation, as shown in Figure 16. The outermost region consists of a thin, dense skin layer ($\sim$ 0.1 μm) supported by a tightly packed nodular transition layer ($\sim$ 0.3 μm) and a highly porous substructure, as shown in Figure 17. Since the O_2/N_2 selectivity of these membranes was within 85% of the intrinsic selectivity of the membrane material, it can be concluded that the fusion of the surface nodules was essentially completed during the evaporation and quench steps.

It is important to note that free-standing evaporation times longer than 60 sec resulted in a dramatic reduction in pressure-normalized oxygen flux without a significant increase in selectivity. Membranes quenched after a 90-sec evaporation period showed a tenfold decrease in pressure-normalized oxygen flux compared to those quenched after 60 sec evaporation. The cross-section of these membranes consists of a sponge-like, essentially macro-void-free substructure (Fig. 18). As expected, the outermost region shows a drastically different structure compared to membranes quenched at shorter evaporation times, as shown in Figure 19. The skin layer appears to be approximately 0.6 μm thick and, even more striking, the underlying region consists of a tightly packed cell-like structure, not
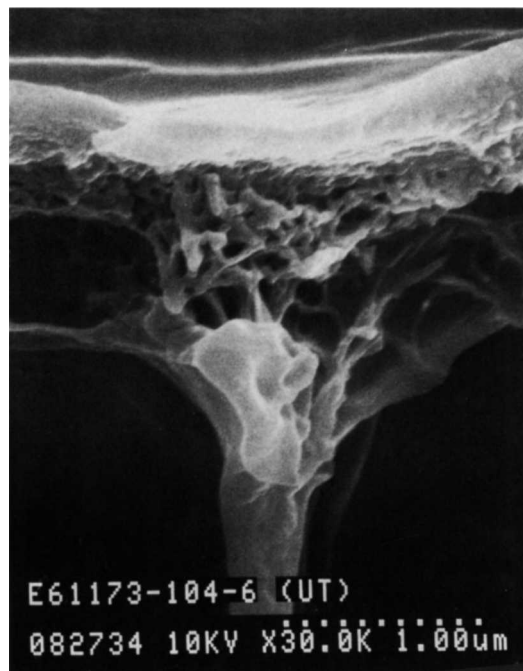

Figure 17 Top structure of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 60 sec. Magnification 30,000×.

seen in membranes quenched at shorter evaporation times than 90 sec. It is suggested that the unique structure of these membranes was generated during the prolonged evaporation period, resulting in deformation and fusion of structures seen in membranes quenched at shorter evaporation times.
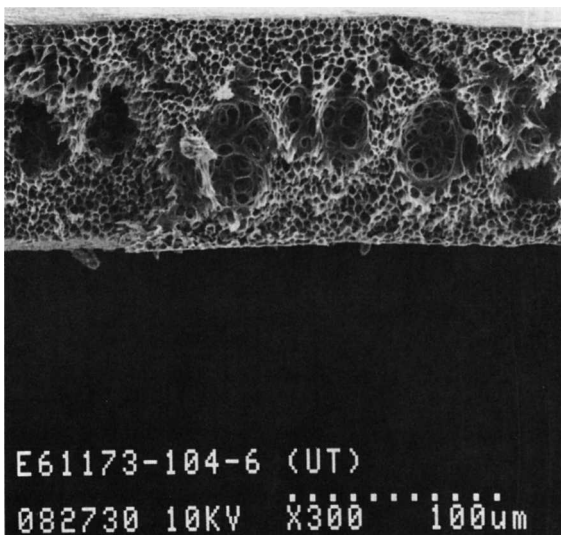

Figure 16 Cross-section of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 60 sec. Magnification 300×.

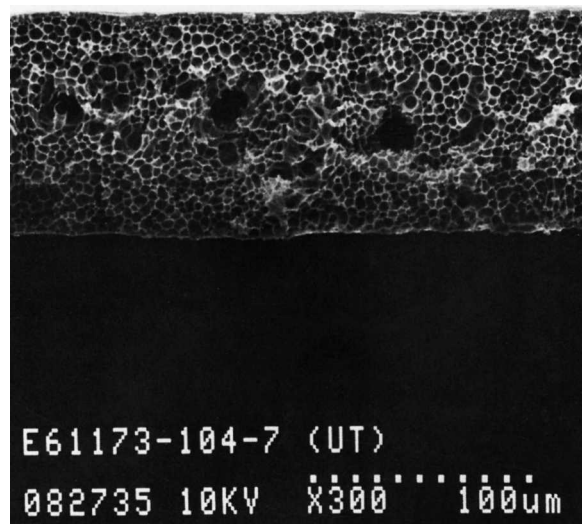**Figure 18** Cross-section of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 90 sec. Magnification 300×.
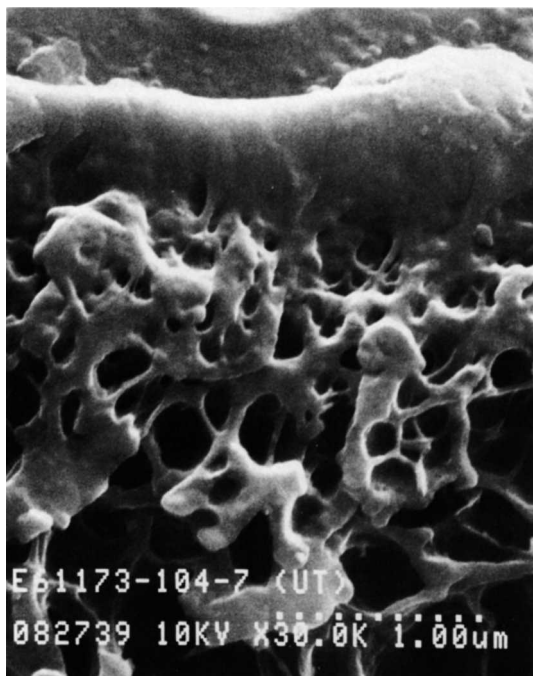
Figure 19 Cross-section of an asymmetric polysulfone membrane made by dry/wet phase inversion. Evaporation time 90 sec. Magnification 30,000×.

The above results show clearly that, for the casting formulation of the present study, the optimized dry/wet phase inversion processes generated asymmetric polysulfone membranes with essentially defect-free and ultrathin skin layers. Furthermore, it is important to note that the dry/wet phase inversion process using convective evaporation is also applicable to the formation of defect-free membranes from a variety of glassy polymers in addition to polysulfone.[31]

CONCLUSIONS

Essentially defect-free integrally skinned asymmetric polysulfone membranes can be fabricated by dry/wet phase inversion processes from a methylene chloride/1,1,2-trichloroethane/2-methyl-2-butanol casting system quenched in methanol. Optimum dry/wet phase inversion membranes consist of an ultrathin skin layer, a tightly packed nodular layer, and a sponge-like substructure. The evaporation kinetics of solvent components during the dry phase inversion step determine the gas separation properties and membrane structures to a large extent. Optimum gas separation performance of dry/wet phase inversion membranes was achieved by convective evaporation-induced interfacial phase sep-

aration prior to the quench step. Free-standing evaporation-induced interfacial phase separation also resulted in essentially defect-free membranes; however, pressure-normalized oxygen fluxes were 1.8 times lower compared to those obtained for dry/wet phase inversion using convective evaporation. It must be noted that the results presented here provide only a first basis to completely understand the physical principles involved in the formation of dry/wet phase inversion membranes. We suggest that the skin formation mechanism of dry/wet phase inversion membranes by the methods described here is of a different physical nature compared to that of membranes made by wet phase inversion. A qualitative skin formation mechanism for dry/wet phase inversion membranes has been proposed.[32] A future publication will focus exclusively on physical processes occurring during the skin formation of dry/-wet phase inversion membranes.

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