

Composite Hollow Fiber Membranes

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Synopsis

Composite polysulfone hollow fibers consisting of a polysulfone porous substrate coated with crosslinked polyethyleneimine (PEI) or furan resin are reported. These composite hollow fibers are analogous to the flat-sheet composite membranes known as NS-100 and NS-200. The surface structure of the porous substrate was rigorously studied before and after coating. Scanning electron microscope observations and reverse osmosis transport studies showed that the support fiber must have surface pore diameters of less than $0.2\ \mu\text{m}$ to obtain a durable composite hollow fiber membrane. The curing process would normally follow in situ condensation of the PEI or the cationic polymerization of the furfuryl alcohol. However, since both the dense layer and surface of the porous substrate contract when exposed to the curing temperature ($110\text{--}150^\circ\text{C}$), it was found to be profitable to cure the hollow fiber before applying the coating. When tested in a reverse osmosis rig, PEI/TDI-coated polysulfone hollow fiber bundles displayed 98% salt rejection and a flux of 5–7 gfd for a feed solution of 10,000 ppm NaCl at a hydraulic pressure of 400 psi. A new method of depositing furan resin on the polysulfone hollow fiber is described. The furfuryl alcohol is instantaneously polymerized by exposing the alcohol-soaked fiber to a 60% solution of concentrated sulfuric acid. It has been demonstrated that in such a polymerization procedure a dense, semipermeable layer is formed on top of the porous substrate; the resulting composite hollow fiber membrane yields salt rejections higher than 98% when tested under the above reverse osmosis conditions.

INTRODUCTION

Porous polysulfone in the form of flat sheets or hollow fiber membranes has been widely used in ultrafiltration processes. Because of its superb mechanical qualities and chemical stability, polysulfone is useful as the porous component upon which ultrathin, dense, semipermeable membranes can be deposited. In this form, the polysulfone substrate serves as the support component in so-called composite membranes. Such membranes have been reported to be very effective for desalination of brackish water and seawater in high-pressure reverse osmosis processes.

Composite flat-sheet membranes have been described by Cadotte et al.,¹ who originated the composites NS-100 (polyurea/polysulfone) and NS-200 (furan resin/polysulfone); by Riley et al.,² who reported on the PA-300 membrane (polyetheramide/polysulfone), and by Yasuda,³ who employed plasma techniques to coat polysulfone substrates. When tested for desalination applications, these flat-sheet composite membranes proved to perform at pressures up to 1500 psi, yielding salt rejections of up to 99.8%. The analogous NS-100 and NS-200 composite hollow fiber membranes have been briefly described by us⁴ and by Allegrezza et al.⁵ The former results from an in situ condensation of polyethyleneimine (PEI) with diisocyanate derivatives, while the latter results from a cationic polymerization of furfuryl alcohol on and within the porous substrate. Both processes require subsequent curing at elevated temperatures, which results in crosslinking and further stabilization of the dense, semipermeable layer.

The present paper elaborates certain aspects of producing a composite hollow

fiber. The spinning, mechanical properties, and morphology of polysulfone hollow fibers have been discussed in previous publications.⁶⁻⁸ It has been shown that polysulfone hollow fibers cannot be spun from the same dope composition used to cast the flat-sheet substrates. Likewise, membrane deposition on the cylindrical fiber requires techniques different from those employed for casting on flat-sheet substrates. The surface structure of the porous support has been rigorously studied and is reported herein.

It was previously reported⁸ that the hydraulic permeability of a hollow fiber is often related to average pore size and pore density. Nonetheless, these dimensional parameters are almost meaningless when the fiber is coated with a dense membrane which displays much higher resistance to water permeation than does the porous substrate. Under the elevated hydraulic pressure applied in reverse osmosis, pore size and morphology at the substrate surface are of major importance. Previous studies have shown⁸ that major changes in surface morphology occur when a wet polysulfone hollow fiber is dried at $\sim 110^{\circ}\text{C}$, which is the curing temperature for the fabrication of the NS-100 composite. Thus, the effects of the curing temperature on the substrate surface and on its ultrathin coating are of major concern and were addressed in the study described here.

EXPERIMENTAL

Spinning of Polysulfone Hollow Fiber

The spinning procedure for polysulfone hollow fibers has been detailed in previous publications.⁶⁻⁷ Briefly, the hollow fibers are spun from a ternary solution of polysulfone (PS), poly(vinylpyrrolidone) (PVP), and dimethylacetamide (DMA). The total polymeric concentration in the solution is 40–52 wt-%, while the preferred ratio of PS/PVP is 1.5–2.0. The tube-in-tube jet technique is used for the spinning procedure. The preferred outside quench medium for the fibers is water at 21°C . The quench medium in the center of the fiber is air or a DMA/water solution. Quenching is followed by washing with hot water ($50\text{--}60^{\circ}\text{C}$). The hydraulic permeability, wall thickness, and fiber diameter are controlled by varying the solution composition, extrusion rate, take-up rate, spinning and quench temperatures, and quench media.⁶

The hydrophobic polysulfone fibers were quenched in a water solution that contained 0.1 wt-% sodium dodecyl sulfate to improve wettability. In some cases, the fibers were washed and stored in the same solution following quenching. Various methods were investigated to improve fiber wettability and surface adhesion properties toward several coating materials. For example, a fiber consisting of a blend of polysulfone and sulfonated polysulfone was produced. The sulfonated PS was used in its acidic form ($-\text{SO}_3\text{H}$) and contained 0.2 meq/g dry charge density. This fiber was spun in the same fashion described above. The dimensions and hydraulic permeabilities (L_p) of several polysulfone hollow fibers are shown in Table I.

Deposition of PEI/TDI (NS-100) and Furan Resin (NS-200) on the External Surface of Polysulfone Hollow Fibers

Material. Polyethyleneimine (PEI-1000 and Tydex 12, Dow Chemical Company), 4-methyl-*m*-phenylene diisocyanate (Matheson, Coleman and Bell),

TABLE I
 Characteristics of Porous Polysulfone and Polysulfone/Sulfonated Polysulfone Blend Hollow Fibers^a

Sample	Composition	Viscosity of spinning solution, cP at 50°C	Fiber internal diameter, μm	Wall thickness, μm	Hydraulic permeability L_p , (cm/sec-atm) $\times 10^5$	Maximum surface pore diameter, μm
3-14-1	Polysulfone	234,000	91	97	32	0.33
3-14-2	Polysulfone	234,000	92	86	36	2.2
3-14-3	Polysulfone	234,000	88	75	26	
4-11-1	PS/Sulfonated PS	76,000	91	91	51	1.4
4-11-2	PS/Sulfonated PS	76,000	95	97	55	0.3
4-11-3	PS/Sulfonated PS	76,000	95	98	60	

^aThe hydraulic permeabilities were determined on air-dried fiber (21°C) by a method described previously.⁷

toluene diisocyanate (BASF Wyandotte Corp.), and hexane (reagent grade, CaCl₂ dried) were used. A solution of PEI was prepared by stirring 2 wt-% Tydex 12 and 2 wt-% PEI-1,000 in water for 24 hr. A solution of 4-methyl-*m*-phenylene diisocyanate was prepared daily by dissolving the required amount in dry hexane. Toluene diisocyanate (TDI) was prepared in the same way. Furfuryl alcohol (tech. grade) was used.

Coating. Polysulfone hollow fibers were coated with polyethyleneimine followed by a crosslinking reaction with *m*-toluene-2,4-diisocyanate and heat curing at 110°C. This coating procedure corresponds with the North-Star¹ method of coating flat sheets of polysulfone porous support. However, the coating technique was adapted to accommodate the hollow fiber structure: The fibers were rolled into a PEI solution and were removed from the solution vertically in such a manner as to avoid the formation of droplets around the fiber due to surface tension. The fiber was allowed to drain and was then dipped into the TDI solution for a specified time. The coated fiber was allowed to air dry for 10 min before it was placed in an oven at 100–110°C for 10 min. Furan resins were coated via the polymerization of furfuryl alcohol (4 wt-% water solution) by sulfuric acid (2 wt-%) followed by curing at 150°C. Modifications of this method and the various polymerization formulations are discussed in the following sections.

Detection of Coating Imperfections

A dye staining technique was used to confirm the presence and uniformity of the PEI/TDI coating. DuPont textile identification stain No. 4 and American Cyanamid Calco stain No. 2 were used. Wet, coated fibers were dipped into a 1% aqueous dye solution at 95°C. Uncoated areas were immediately stained dark blue (absorbed the original dye mixture into the pores), while the polyurea surface was dyed an orange-yellow (Fig. 1). Variations in the bluish hue constitute an adequate qualitative check of the pore size and pore density at the substrate surface.

Another method of detecting imperfections in such coated fibers is to observe a penetrating front of hexane into a dry fiber wall. Such tests are performed by placing a sample of plugged fiber into a Petri dish containing hexane. Because the refractive index of hexane is close to that of the base polysulfone, the hexane-filled fiber is transparent. Since the absorption of hexane in the uncoated fiber is very fast compared to the penetration of hexane through the PEI layer, the uncoated regions become transparent while the coated segments remain opaque. A stereomicroscope is used to examine the fibers.

Experimental Bundle Assembly (Fig. 2) and Testing

The evaluation of composite hollow fiber bundles is often complicated by the difficulty of determining whether fiber faults developed during the coating steps or were created during the assembly and potting steps. Therefore, small ten-fiber bundles were employed for testing, and precautions were taken to assure minimal damage during potting. The following procedure was employed: A bundle of ten coated fibers was passed through a 7½-in. length of polyethylene tubing, leaving approximately equal lengths of fiber extending on both ends of

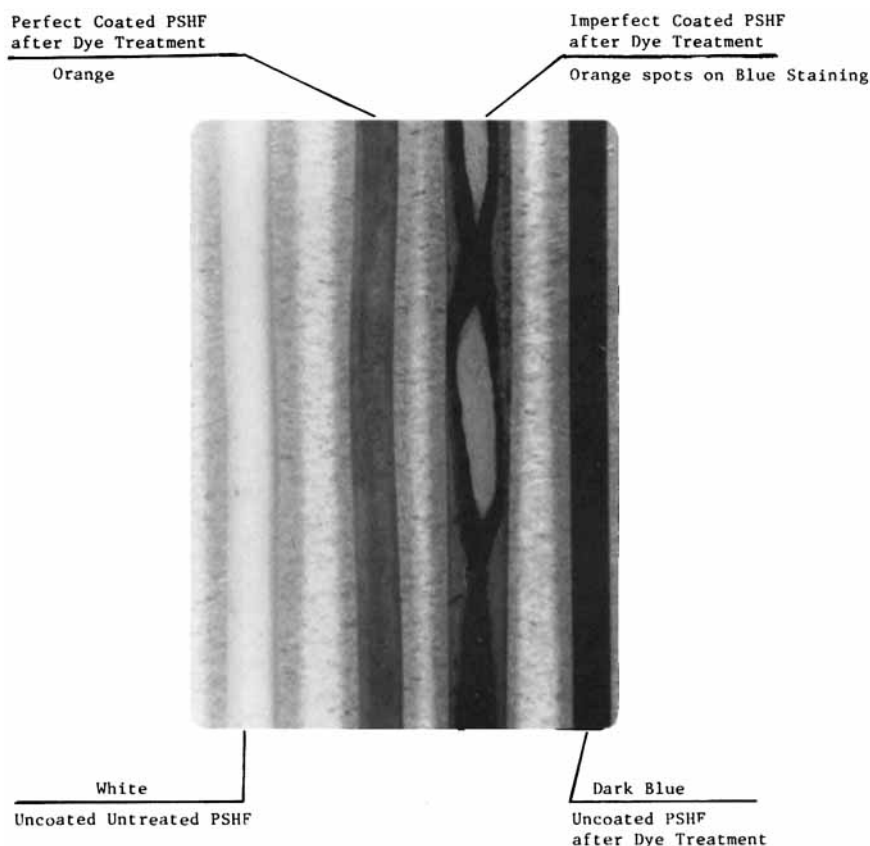
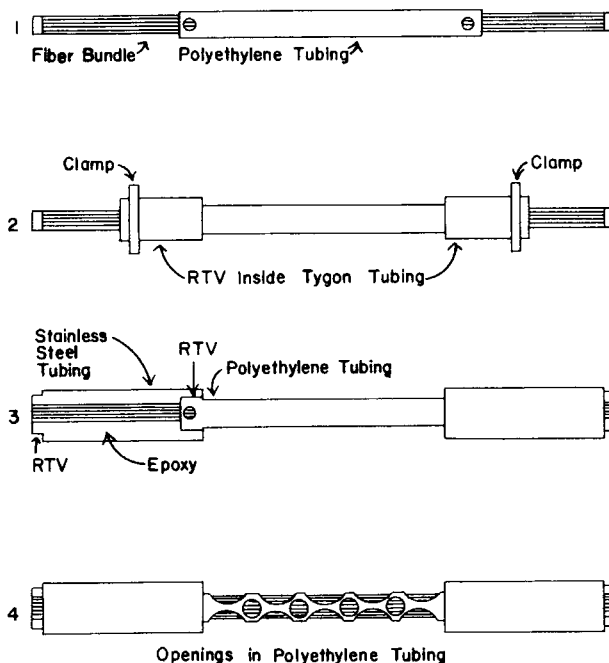


Fig. 1. Dye test of uncoated and coated (PEI/TDI) polysulfone hollow fiber. (Dye: du Pont textile identification stain No. 4.)

the tubing. Two 2½-in. lengths of Tygon tubing were fitted and fastened with small clamps as shown in the figure. That portion of the Tygon tubing from the clamp to the center of the assembly was filled with RTV potting compound and allowed to cure. When cured, the clamps and the Tygon tubing were removed and the RTV plugs cleaned and shaped. Each RTV plug was wrapped with a thin film of polyethylene and pressed into a 3½-in. length of ⅜-in. diameter stainless steel tubing. To protect the fibers from rough edges, another piece of Tygon tubing approximately 1 in. long was inserted into the end of the steel tubing. The whole empty compartment of the stainless tubing was then filled with epoxy resin. After the epoxy cured, the outside tips of the Tygon tubing were filled with RTV to improve flexibility at the ends of the fibers. The central polyethylene tubing was then cut to give maximum exposure to the feed saline solution. By using such a bundle, single fibers can be sampled as conveniently as measuring the total group. The polyethylene tube protects the fiber against stretching and bending, and the RTV potting eliminates fiber breakage near the brittle epoxy end.

In addition to the ten-fiber test bundles, bundles containing 100 fibers each were prepared as reverse osmosis operating units. These bundles were inserted into stainless steel tubes for tests under elevated hydraulic pressures.^{6,9} A feed solution of 10,000 ppm NaCl was employed at a flow rate of 1–3 gpm.

POTTED FIBER FABRICATION SCHEME



Stainless Steel Tubing: 3/8 in.
 Tygon Tubing: 7/16 in. O.D., 1/16 in. Wall

Fig. 2. Experimental bundle fabrication scheme.

RESULTS AND DISCUSSION

The polysulfone hollow fibers listed in Table I have an asymmetrical morphology which is the result of anisotropic coagulation of the spinning solution.⁷ The fiber wall consists of a highly porous external skin (~ 250 Å thick) resting on a highly porous sponge structure which has a lower density (50%–70% void volume) than the skin.

In previous studies^{7,8} it was demonstrated that the surface of the polysulfone hollow fiber could be affected by exposure to temperatures in the range employed for curing NS-100 and NS-200 composite membranes (100–150°C). A drastic surface pore contraction occurs through this temperature range which, however, only marginally affects the fiber hydraulic permeability.⁷

The diverse effects of temperature on a polysulfone hollow fiber surface are demonstrated in Table II and Figure 3. Exposure to temperatures above 150°C for extended periods of time leads to structural changes and collapse of capillaries in the internal sponge layer. Thus, even though the surface pores seem to reenlarge at 150–170°C (Fig. 3), the collapse of the inner structure results in a substantial decrease in hydraulic permeability. At temperatures above 170°C, a dense, nonporous, transparent hollow fiber is formed. The effects of curing temperature must therefore be taken into account whenever an ultrathin, semi-permeable membrane is to be deposited on a porous polysulfone substrate.

The relationship between surface pore diameter and the thickness of the deposited dense layer must also be considered. The surface of an uncoated and

TABLE II
Surface Structure of Heat-Treated Polysulfone Hollow Fiber

Fiber designation	Temp., °C	Time, min	Maximum pore diameter, μm	Average pore diameter, ^a μm	Hydraulic permeability L_p , (cm/sec-atm) $\times 10^5$
3-14-1	20	—	0.33	0.09 ± 0.03	32
3-14-1a	120	30	0.12	0.04 ± 0.01	
3-14-1b	150	10	0.09	0.04 ± 0.01	27
3-14-1c	150	20	0.1	0.05 ± 0.01	
3-14-1d	150	30	0.17	0.07 ± 0.02	
3-14-1e	160	30	0.25	0.15 ± 0.1	5
3-14-1f	170	60	0.03	< 0.1	0

^a At least 60% of the observed pores fall within the reported ranges.

that of a PEI/TDI-coated polysulfone hollow fiber are shown in Figure 4. The initial pore dimensions of this fiber are relatively large ($\sim 0.5 \mu\text{m}$). During heat treatment the pores, which are filled with coating material, undergo dimensional reductions, forcing the ultrathin layer up and forming a mounded surface. This is clearly shown in Figure 5, where cross sections of coated and uncoated hollow fibers are shown. It can be seen that the polyethyleneimine (PEI) fills the surface pores and that there is a "mound" above each pore. However, a relatively flat surface is obtained when the pore diameter is small in relation to the coating

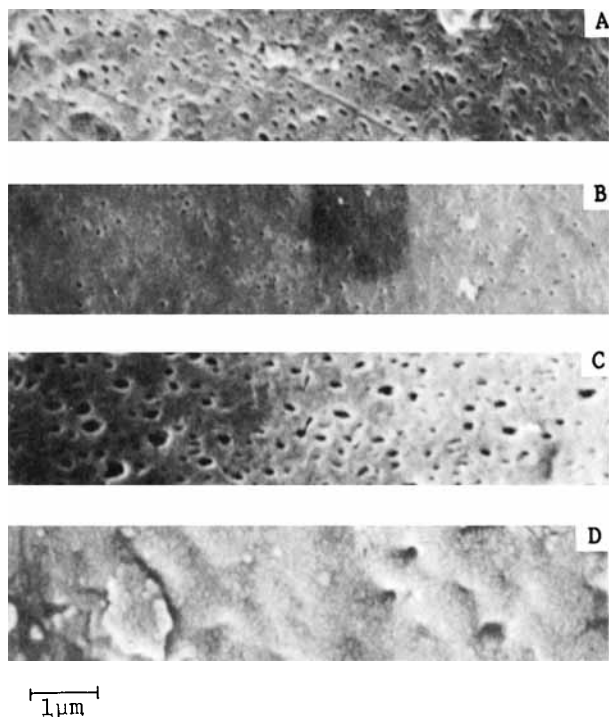


Fig. 3. Effect of heat treatment on surface structure of porous polysulfone hollow fiber spun from a dope composite of PS/PVP/DMA: (a) air dried at 21°C ; (b) cured at 120°C for 20 min; (c) cured at 160 – 170°C for 20 min; (d) cured at 170°C for 60 min. Hydraulic permeabilities of the above fibers, L_p , in (cm/sec-atm) $\times 10^5$, are 32, 27, 5, and 0, respectively.

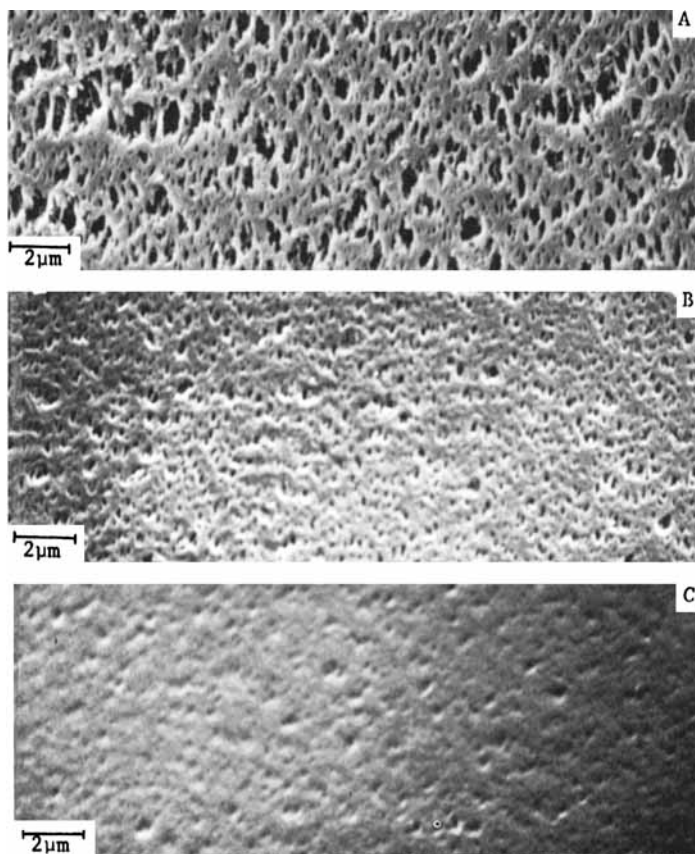


Fig. 4. Surface structure of polysulfone hollow fiber: (a) air dried 21°C; (b) oven dried 110°C (10 min); (c) PEI/TDI coated and then cured at 110°C (10 min).

thickness, as shown in Figure 6. In this case the coated layer displays a wavy pattern (which is also often observed when examining the dense skin of cellulose acetate asymmetric membranes).

The crosslinking of the polyethyleneimine dense layer is accomplished chemically by the TDI and thermally by the subsequent heat treatment. Microscopic observation of a hexane front penetrating into a PEI-coated hollow fiber reveals that the TDI crosslinking reaction occurs mainly on the upper surface of the PEI coating. Once chemically crosslinked, this layer serves as a barrier to the penetration of nonpolar solvents such as hexane. However, a hexane/TDI solution penetrates this layer more easily since the TDI, a polar species, is absorbed better in the PEI matrix. The resistance to a hexane penetrating front was measured only semiquantitatively and seems to follow the trend

$$PEI_{(TDI/T)} > PEI_{(TDI)} > PEI_T > PEI$$

For this purpose, the polysulfone hollow fiber was coated with 2 wt-% Tydex-12, crosslinked with 1 wt-% TDI in hexane, and dried at 21°C. When the fiber was thermally treated (designated above as T), the conditions were 10 min at 110°C.

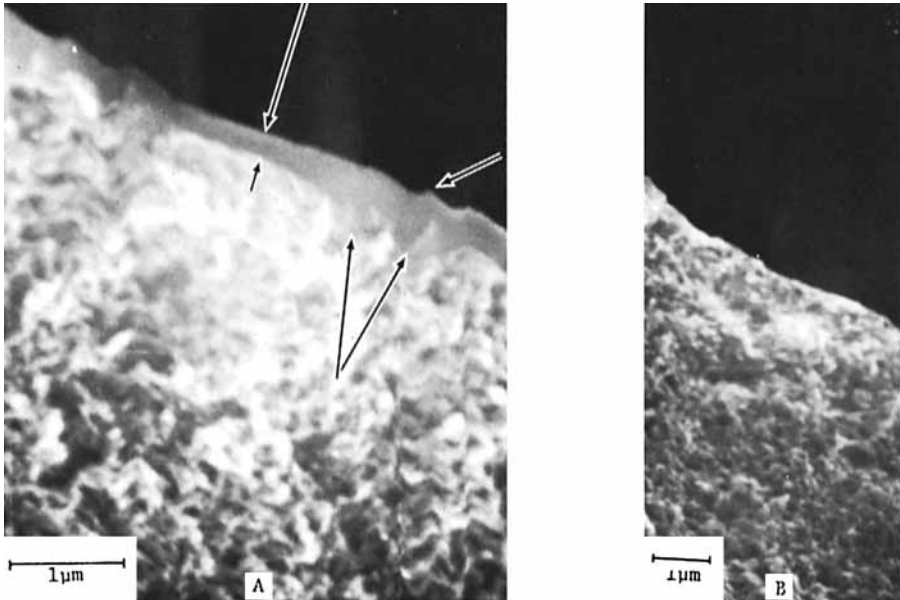


Fig. 5. Cross sections of coated (a) and uncoated (b) polysulfone hollow fiber. The PEI-filled pores, thickness, and shape of the cured ultrathin membrane are indicated by the arrows.

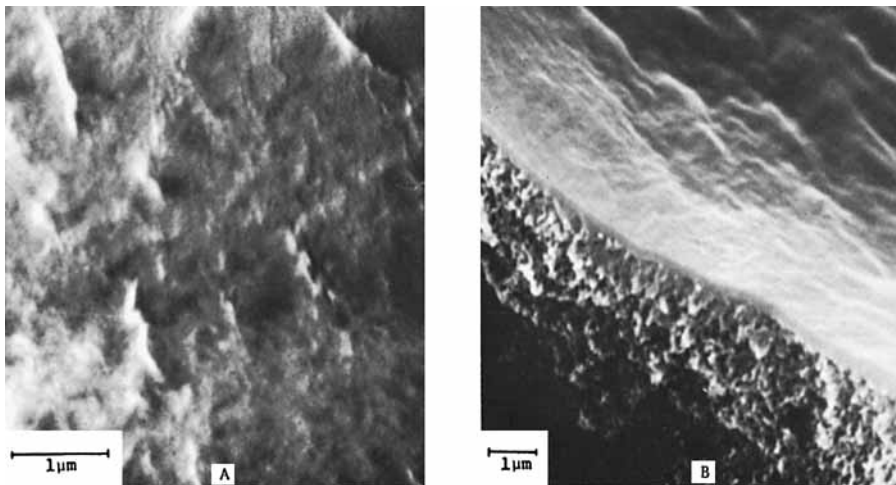


Fig. 6. Composite polysulfone hollow fiber: (a) surface structure of PEI/TDI ultrathin dense coating; (b) cross section displaying an ultrathin dense layer resting on a porous substrate.

Simultaneously with the contraction of the surface pores during the thermal treatment, there are substantial dimensional changes in the PEI-coated layer, which also contracts as a result of thermal crosslinking. In this regard, care must be taken to minimize mismatch between the structural changes that occur in the heat-treating stage. It was found that if the fiber is held under tension during heat treatment (for example, as when composite fiber is produced in continuous fashion, being run through a heating tube), contraction forces may increase the tension and rupture the ultrathin coating. As a result of this observation, thermal treatment of the fibers was always carried out on untensioned fibers.

During the first stage of this study, coating was applied on wet (never dried) fibers. The overall thickness of the PEI/TDI layer ranged between 0.1 and 0.3 μm (Figs. 5 and 6). Reverse osmosis tests conducted on the composite fibers indicate that when the surface pore diameters are greater than the thickness of the semipermeable coating, salt rejections are poor (<60%). When subjected to elevated hydraulic pressure, the coating was punctured, as is clearly shown by scanning electron microscopy (Fig. 7). The composite fiber designated 4-11-2, which has surface pore diameters in the range of 0.1–0.2 μm , exhibits salt rejections greater than 80%. The best performance of this composite fiber (when wet coated) was a 92% salt rejection corresponding to a flux of 7 gfd at a pressure of 400 psi. The above results, drawn from tests of 100 test bundles, indicate that even though the PEI coating fills the surface pore (Fig. 5), the surface pore diameter should be less than 0.2 μm in order to obtain a durable composite hollow fiber for reverse osmosis.

Deposition of Coating on Heat-Treated Fibers

The above results, which demonstrate the effect of heat treatment on the fiber surface, prompted an attempt at depositing the dense, semipermeable coating on dry, preconditioned, heat-treated fibers. Dry polysulfone hollow fiber is vulnerable to organic liquids such as the TDI/hexane solution. The fiber rapidly absorbs the organic solution into its matrix, and substantial dimensional changes occur almost instantaneously. This is the case even with exposure to nonpolar solvents, such as hexane, because the porous substrate displays an extremely high ratio of surface area to polymer (material). Even short exposure times result in enough absorption, into the polymeric matrix to affect the overall morphology.

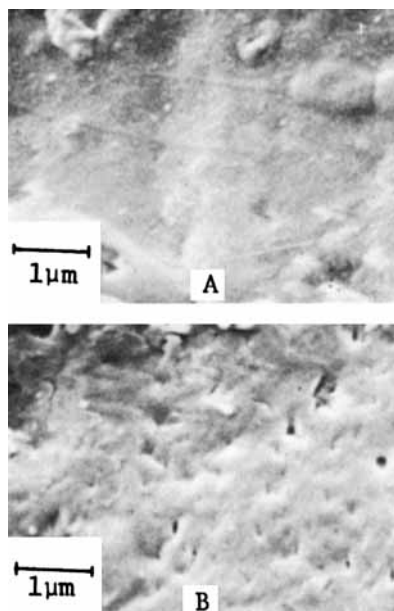


Fig. 7. Composite polysulfone hollow fiber (PEI/TDI coated) after exposure to reverse osmosis testing (pressures up to 1000 psi; feed, 10,000 ppm NaCl): (a) displays an intact surface yielding 98% salt rejection; (b) punctured surface resulting from highly "mounded" coating.

TABLE III
Effect of Immersion Time in Hexane/TDI on PEI/TDI-Coated Composite
Polysulfone Hollow Fibers^a

Immersion time, sec	Water flux, gfd	Salt rejection, ^b %
15	200	7
30	8	98
45	2	97
90	fiber collapse	—

^a Coating procedure: polysulfone hollow fiber designated 4-11-2 was oven dried at 120°C for 20 min. The fiber was immersed for 1 min in a PEI water solution (2 wt-% Tydex 12 + 2 wt-% PEI-1000) which was maintained at pH 10.8. The fiber was then immersed in hexane/TDI solution, allowed to dry, and then cured for 10 min at 120°C.

^b For a feed solution of 10,000 ppm NaCl, applied hydraulic pressure 400 psi.

Immersion of a dry fiber in the water/PEI solution for 1 to 10 min during the first coating stage does not prevent the hexane solution in the second stage from diffusing rapidly into the fiber matrix. When the coating procedure is applied to a wet fiber, the fiber is protected since the water phase shields the polymeric matrix. However, once dried, it takes a long time for such a hydrophobic network to imbibe to saturation and thus become resistant to the swelling effect of the

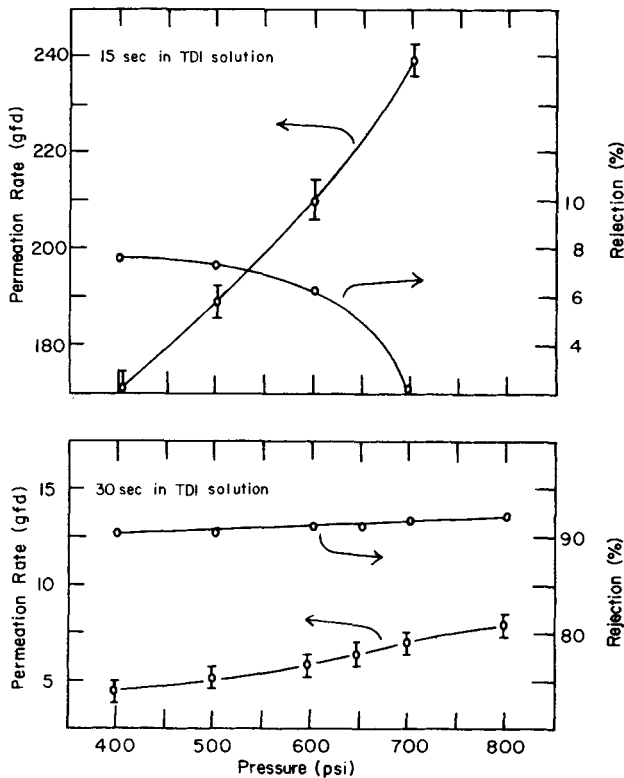


Fig. 8. Permeation rate and salt rejection vs. pressure for PEI/TDI-coated fibers. Condensation of the PEI was carried out with 1 wt-% TDI in hexane solution.

TABLE IV
Effect of Heat Treatment on Performance of PEI/TDI-Coated Polysulfone Hollow Fiber^a

Fiber designation	Untreated			Heat-treated		
	Average pore diameter, μm	Salt rejection, %	Flux, gfd	Average pore diameter, μm	Salt rejection, %	Flux, gfd
3-14-1	0.093	—	—	0.057	97	1.5
3-14-2	0.162	77	15	0.09	98	7
3-14-2a	0.692	20	60	0.231	84	7
4-11-1	0.35	30	45	0.18	93	7
4-11-2	0.183	92	7	0.095	97	5

^a Reverse osmosis test conditions: solution, NaCl 10,000 ppm; pressure, 400 psi; temperature, 20°C

hexane/TDI solution. It was found that the fibers designated 4-11, which are PS \neq sulfonated PS blends, show higher hydrophilicity and better resistance to hexane swelling effects than do the fibers designated 3-11.

The effect of hexane/TDI solution on the heat-treated fiber is shown in Table III and Figure 8. In these examples, fiber 4-11-2 was heat treated for 20 min in a 120°C oven and subsequently immersed for 1 min in PEI solution (2% Tydex 12 + 2% PEI-1000, pH 10.8) and for required periods of time in TDI solution (4% in hexane) followed by curing at 120°C for 10 min. The results show that the PEI/TDI ultrathin membrane can be successfully deposited on dry polysulfone hollow fiber. However, care must be taken with the immersion time in the

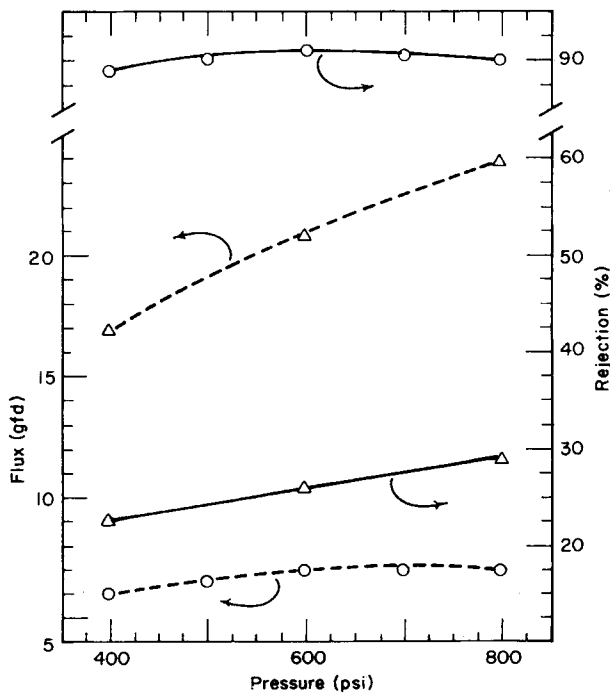


Fig. 9. Flux rates and salt rejections vs pressure for heat-treated (O) and untreated (Δ) PEI/TDI-coated polysulfone hollow fibers.

TABLE V
The Effect of Rewetting on the Performance of Heat-Treated PEI/TDI Coated Polysulfone Hollow Fibers^a

Rewetting time, hr	Salt rejection, %	Flux, ^b gfd
0.0	94	2.9
0.5	94	2.0
12	93	2.8
14 days	94	3.1

^a The fiber (4-11-1) was heat treated at 150°C for 20 min, coated by the standard procedure, and immersed in water as indicated. The results are for the initial 20 min of testing.

^b Reverse osmosis test conditions: solution, NaCl 10,000 ppm; pressure, 400 psi; temperature, 21°C.

hexane/TDI solution. It is not yet clear why an immersion time of 15 sec gave such poor results. Salt rejections higher than 25% could not be achieved with any dry polysulfone hollow fiber that was immersed in the TDI solution for less than 18 sec.

The heat treatment of the polysulfone fibers led to a substantial improvement in the overall performance of the composite fibers, as demonstrated in the results shown in Table IV and Figure 9. Also, the correlation between surface pore size

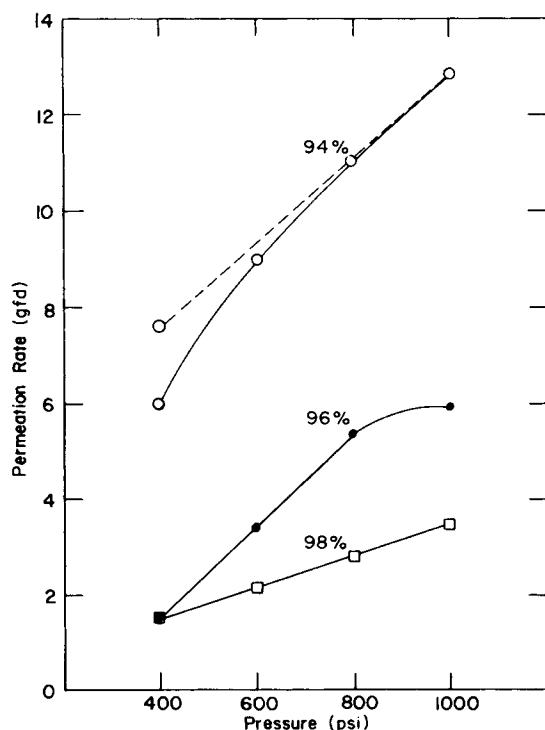


Fig. 10. Permeation rate vs pressure. Linear relationship is shown for the first composite fiber (98% SR), irreversible compaction at 600–800 psi for the second (96% SR), and a typical initial transport curve (solid line) which upon equilibration displays the linear relationship shown by the dotted line (94% SR). Feed solution for the test, 10,000 ppm NaCl.

and composite fiber performance is evident. These data confirm that the average surface pore size of the support fiber should be less than $0.2\ \mu\text{m}$ in order to achieve adequate performance ($>90\%$ salt rejection). The fiber designated 4-11-2, which fulfills this requirement, displays high salt rejection without heat treatment. However, its performance improved substantially when the fiber was heat treated.

Rewetting the dry, composite hollow fiber by immersing the fiber bundle in water prior to testing seems to have marginal influence, if any, on fiber performance. However, steady-state performance was reached faster with the more hydrophilic fibers (the sulfonated PS blends); for the others it took up to 45 hr to reach a steady-state flux. Hollow fiber bundles that were immersed in a water bath for up to one month before testing displayed the same average flux rate and salt rejection as did fiber bundles that were mounted dry in the reverse osmosis rig. Similar results were found for all polysulfone hollow fiber composites of this type that were heat treated before coating (Table V).

In general, test results show a linear correlation between flux and the applied hydraulic pressure when operated under reverse osmosis conditions. Three typical curves are shown in Figure 10. The first (98% solute rejection) shows no compaction as a result of the progressively increased pressure. The second exhibits a linear increase in flux up to 800 psi; higher pressure results in irreversible compaction and a decrease in the water permeation rates. The solid line of the upper curve (salt rejection, 94%) shows the typical response of a nonequibrated composite membrane to the elevated hydraulic pressure. After equilibration, the fiber establishes a linear transport characteristic, as shown by the dotted line.

None of the composite polysulfone hollow fibers that were coated with PEI/TDI (less than 40 sec of exposure to the hexane/TDI solution) showed any catastrophic collapse when exposed to hydraulic pressures up to 1200 psi.

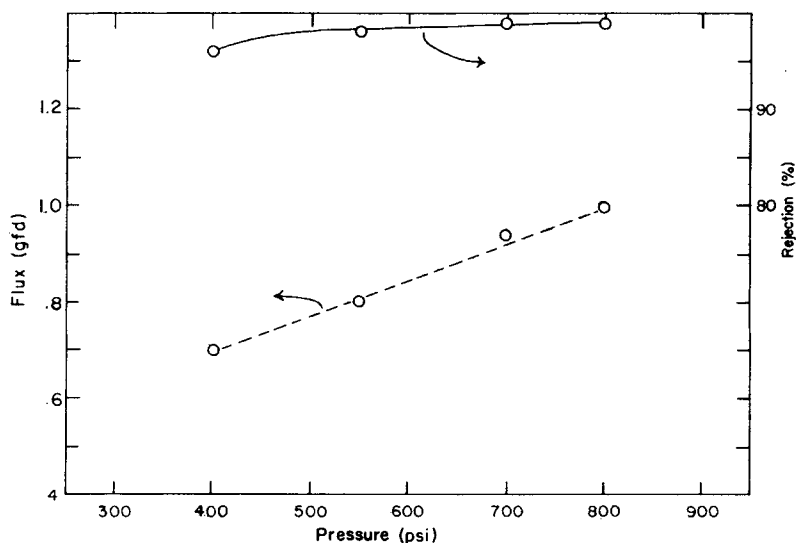


Fig. 11. Flux rate and salt rejections vs pressure for furan resin-coated polysulfone hollow fibers (feed solution, 10,000 ppm NaCl).

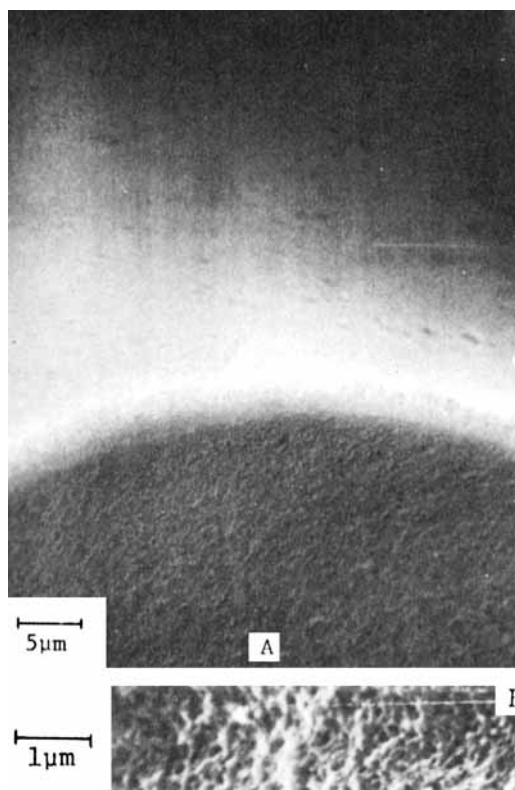


Fig. 12. Furan resin-coated polysulfone hollow fiber: (a) cross section; (b) surface structure of the coating preexposed to reverse osmosis test.

Furan Resin Deposition

Cationic polymerization of furfuryl alcohol on a porous polysulfone support forms a selective membrane on (or within) the support. High separation of salt from water accompanied by high water transport was reported by Cadotte et al.¹ Applying the coating procedure formulated by these investigators on the polysulfone hollow fibers resulted in very poor salt rejections under reverse osmosis test conditions. Numerous reverse osmosis runs on different types of fiber bundles have resulted in an average of only 10% salt rejection. The composition of the initial coating solution was¹ water, 75.3 wt-%; isopropyl alcohol, 20.0 wt-%; dodecyl sodium sulfate, 0.7 wt-%; sulfuric acid, 2.0 wt-%; and furfuryl alcohol, 2.0 wt-%.

The porous support was soaked in the solution and then cured in an oven at an elevated temperature ($\sim 150^{\circ}\text{C}$). At this temperature, the water evaporates and the sulfuric acid, which progressively concentrates, reacts rapidly to form a furan resin coating. Studies carried out by us showed that the H_2SO_4 also reacts with the polysulfone aromatic ring to form a charged sulfonated polysulfone ($-\text{SO}_3\text{H}$).¹⁰ The coating solution, which contains the furfuryl alcohol and the sulfuric acid in one mix, is unstable, and polymerization of the furfuryl alcohol occurs at a slow rate. Even at low acid concentrations, the lifetime of the solution is 15 to 60 min (at room temperature). A thorough study of the relationship between the furfuryl alcohol polymerization solution and the morphology of the

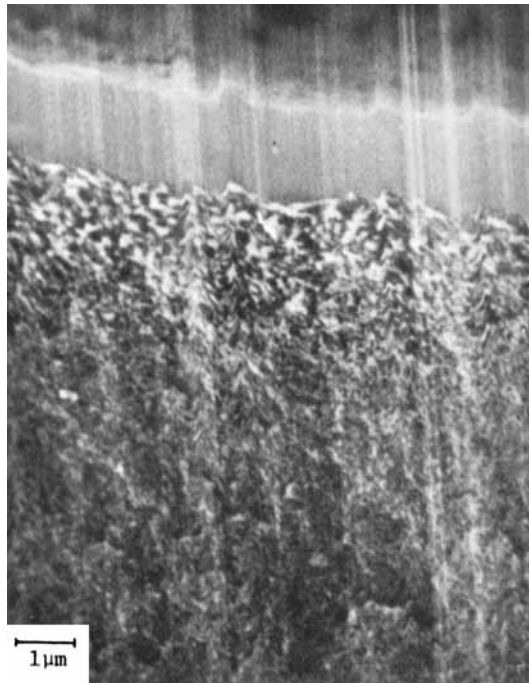


Fig. 13. Furan resin membrane, resting on polysulfone porous hollow fiber. This cross section was taken after testing the fiber. Transport characteristics are shown in Figure 11.

substrate surface clearly indicates that polymerization occurs as deep as $2\ \mu\text{m}$ into the polysulfone surface.¹⁰ Since there is a definite interaction between the substrate polymer and the sulfuric acid, simultaneously with the cationic polymerization of the furfuryl alcohol, it was found that (1) the fraction of the furfuryl alcohol (in the coating solution) should be increased as the surface pore size increases, and (2) the means by which the temperature is elevated (rate at which sulfuric acid concentration increases) is most important in obtaining a continuous resinous film within the surface matrix. A perfect ultrathin film can be obtained by curing the solution in a microwave oven¹⁰ instead of heating the fiber in conventional oven or heating tubes (as in the continuous fabrication of composite hollow fibers).

The following formulation was found to be adequate for coating the heat-treated fiber designated 4-11-2: water, 76–81 wt-%; methanol 16–20 wt-%; isopropanol 2–4 wt-%; and furfuryl alcohol 4–6 wt-%. Wetting agents, such as dodecyl sodium sulfate, seem to have negative effects on the selectivity of the composite membrane and were excluded. Salt rejections up to 98% accompanied by flux rates of 1 to 4 gfd (800 psi) were obtained.

Several other methods of depositing a furan resin on polysulfone hollow fibers were studied. The effort was directed toward development of a continuous coating operation in which the fiber draw rate is rapid. The most promising utilized two separate solutions: a furfuryl alcohol solution and a sulfuric acid solution. A water-swollen fiber (3-14-2) was immersed for 10 sec in a solution of 20% furfuryl alcohol in isopropanol. The fiber was then removed from the solution by a technique which prevents the formation of droplets on the fiber

surface and was immediately run through a 60% solution of H_2SO_4 for 30 sec. Polymerization of the furfuryl alcohol was instantaneous and the fiber turned black. The coated fiber was then rinsed with distilled water and the coating procedure repeated. High salt rejections were obtained from composite fibers fabricated in such a procedure, as shown in Figure 11. Scanning electron micrographs of the tested fibers are shown in Figure 12. The furan resin is deposited on the fiber surface at a thickness of up to 2.0 microns. This is a relatively thick membrane, compared to the coating thicknesses of 0.1 to 0.3 μm shown for PEI/TDI. Such a thick coating results in low flux rates, as shown in Figure 11. Higher flux rates were achieved by reducing the concentration of the furfuryl alcohol in the solution. Coating the fibers by the same procedure with a solution of 12% furfuryl alcohol resulted in a flux of 2 gfd, corresponding to applied hydraulic pressures of 500 psi.

The surface structure of the furan resin layer, Figure 12(b), is rather rough. This picture was taken of a composite fiber after exposure to a hydraulic pressure of 1000 psi; the fiber yielded > 98% salt rejection. This rough surface is apparently the result of some compaction that occurred in the dense layer. However, cross sections of such a composite fiber reveal an extremely dense layer (Fig. 13).

The above coating technique is currently under study. The performance of improved composite fibers of this type having a coating thickness of less than 0.2 μm resting on other support materials, will be reported elsewhere.¹⁰

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References

1. J. E. Cadotte, C. V. Kopp, Jr., K. E. Cobian, and L. T. Rozelle, National Technical Information Service, U.S. Department of Commerce, Washington, D.C., PB-234198, 1974.
2. R. L. Riley, R. L. Fox, C. R. Lyons, L. E. Milstead, M. W. Seroy, and M. Tagami, *Desalination*, **19** 13 (1976).
3. H. Yasuda, in *Reverse Osmosis and Synthetic Membranes*, S. Sourirajan, Ed. National Research Council, Canada, Ottawa, 1977, p. 263.
4. I. Cabasso, E. Klein, and J. K. Smith, *Org. Coat. Plast. Chem. Prepr.*, **35**, 492 (1975).
5. A. E. Allegranza, Jr., R. D. Dunchesky, G. Gött, and R. B. Davis, M. J. Coplan, *Desalination*, **20**, 87 (1977).
6. I. Cabasso, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.*, **20**, 2377 (1976).
7. I. Cabasso, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.*, **21**, 165 (1977).
8. I. Cabasso, L. Q. Robert, E. Klein, and J. K. Smith, *J. Appl. Polym. Sci.*, **21**, 1883 (1977).
9. I. Cabasso and C. N. Tran, *New Polymeric Membrane Containing Phosphonate Ester Groups for Desalination*. Office of Water Research and Technology, U.S. Department of the Interior, Washington, D.C., Final Report 6523, November 1977.
10. I. Cabasso, to appear.

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