

Polymer Alloy Membrane. I. Cellulose Acetate-Poly(Bromophenylene Oxide Phosphonate) Dense and Asymmetric Membranes

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Synopsis

Cellulose acetate (CA) and poly(bromophenylene oxide, dimethylphosphonate) (PPOBrP), which are compatible polymers, have been cast from solution to give both dense and asymmetric alloy membranes. Membranes containing PPOBrP with different degrees of phosphonylation have been prepared. The water absorption of these membranes increases with the number of phosphonate ester groups, but is kept in the range of 12–16 wt-% water for most of the alloy compositions, which contained 20–80 wt-% PPOBrP. The morphologies of asymmetric membranes obtained from various casting formulations were studied by scanning electron microscopy. Two different structures were identified: (1) the well-known dense skin resting on an open-celled foam, and (2) skin resting on a porous layer which displays a two-phase morphology. In the latter, dense spheres (0.1–1 μm) appear to grow out of a continuous polymer network. The membranes have been tested for hydraulic permeability and separation of water from salt solutions by reverse osmosis. In general, the asymmetric alloy membranes that had been annealed at 90–95°C display salt rejections >90% and water permeation rates of 10–30 gfd. Since the phenyl ring of the PPOBrP component was brominated prior to membrane fabrication, the membranes exhibit exceptional tolerance to chlorinated water (20–80 ppm), as demonstrated in short-time durability tests. The irreversible collapse of these membranes occurs at applied hydraulic pressures far above 1200 psi. A cross linking between the two polymer components in the membranes and some suggestions for further improvement of these membranes are also reported.

INTRODUCTION

A polymer alloy consists of two or more polymers that are compatible at the molecular level; such an alloy can be solvent-cast under appropriate conditions to form a homogeneous (single-phase) membrane that combines the properties of each polymeric component into a distinct new product. Homogeneous polymer blends are scarce since polymer compatibility is not favored, as can be shown by simple thermodynamic considerations.¹ Exceptions include polymeric systems which display specific interactions. For many applications, the combination of polymer components by copolymerization or graft copolymerization is adequate, and phase or microphase separation is overlooked once the product displays the desired set of properties. However, mass transport in polymer matrices is directly affected by the morphology and chemical uniformity of the material. For example, in a block copolymer having amorphous domains with

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different structures and chemical affinities, it is often difficult to characterize mass transport phenomena, or to tailor a specific semipermeable membrane. This difficulty is especially apparent for mass transport through ultrathin, dense, semipermeable membranes, as in reverse osmosis or in organic liquid mixture separation. For example, if the domains of such a nonhomogeneous polymeric material are larger than the effective membrane thickness, the permeating substance will pass through two different homopolymer networks. While such a condition is sometimes desirable in "mosaic" membranes for piezoelectric transport or if one domain is present only for mechanical reasons, it is of no value, and is in fact detrimental, for most other membrane transport mechanisms.

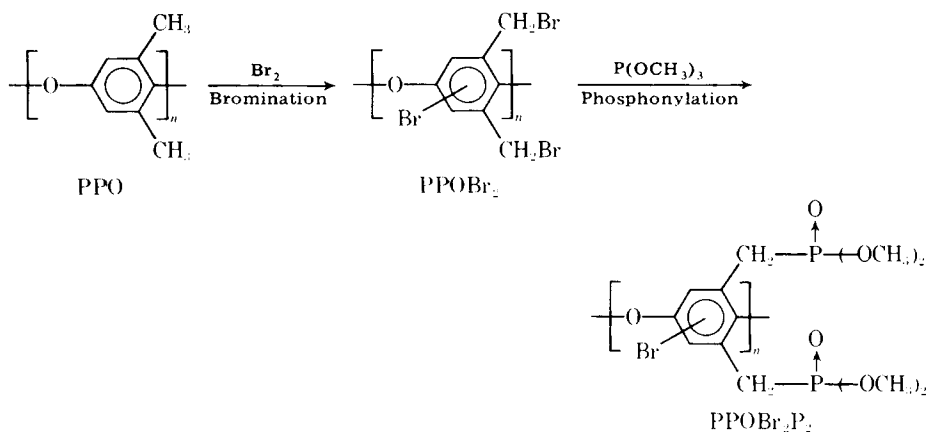
Polymer alloy membranes have been reported to be very effective in separating azeotropic liquid mixtures.^{2,3} It has been shown that the random copolymer (vinylidene chloride-styrene phosphonate) can be easily alloyed with cellulose acetate to give a homogeneous semipermeable membrane by casting the polymers from a mutual solvent. Such a membrane selectively absorbs benzene from benzene/cyclohexane solutions and thus is effectively used in separating the solution components. The source of this alloy membrane characteristic is the affinity of the copolymer (vinylidene chloride-styrene phosphonate) to benzene.

A solvent-cast, dense alloy membrane requires a compatible solvent/polymer system, e.g., the two compatible polymers should be cast from a mutual solvent. As simple as it sounds, such a system is rare. Even rarer are oriented alloy membranes, such as the "asymmetric" membranes. Membranes of this type, introduced first by Loeb and Sourirajan,⁴ are formed by anisotropic gelation of the polymer casting solution. Such a membrane consists of a dense, ultrathin layer resting upon a relatively thick, porous, spongy matrix. The permselectivity is provided by the dense layer, which is mechanically supported by the porous matrix. The formation of such a morphology requires a delicate balance of the multicomponent (polymer/solvent/nonsolvent) system. When more than one polymeric component is involved, the solvent/nonsolvent system must not lead to polymer phase separation at the ultrathin dense layer. Such an asymmetric alloy membrane has been obtained by blending cellulose triacetate with cellulose acetate and is used commercially for the desalination of water by reverse osmosis.⁵ Also, it was reported recently that asymmetric alloy membranes made of polystyrene phosphonate and its copolymers with vinylidene chloride have been successfully cast, yielding flux rates higher than those of the dense isotropic membranes employed for the separation of aromatic from aliphatic liquid mixtures.⁶

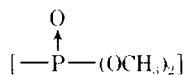
The present paper addresses the development of alloy membranes composed of two polymeric components: ring-brominated poly(phenylene oxide phosphonate) and cellulose acetate. Preliminary studies have shown that this alloy, when cast as a dense membrane, has an outstanding capability to separate alcohols from their azeotropic mixtures with aliphatic hydrocarbons.³ These studies were extended, and the development of asymmetric alloy membranes for desalination of water by reverse osmosis is reported here.

The development of poly(phenylene oxide phosphonate) (PPOP) was previously reported.⁷ Poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) can be modified

as follows:



The pendant phosphoryl ester groups



impart hydrophilicity to the phosphonylated polymer. By altering the degree of bromination and phosphonylation, a hydrophilic–hydrophobic balance can be established in the polymer. As a result of manipulating this balance, water transport through PPOBrP₂ membranes is controllable.

The polymer PPOBrP₂ is a film former, and its characteristics as a Lewis base, due to its phosphoryl groups, permit its interaction as a chelating polymer agent with metal salts^{8,9} and its specific interaction with a variety of polymers.⁶ Compared to the cellulose esters and polyamides used in the fabrication of reverse osmosis membranes, this polymer displays superior resistance to chlorine and can be employed in a wide pH range (1–11) at ambient temperatures. Therefore, the unique compatibility of this polymer with cellulose acetate has been studied with regard to the possible formation of improved reverse osmosis membranes, and is reported here.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide): product of General Electric (Selkirk, N.Y.), $[\eta]^{25^\circ\text{C}}$ chloroform = 0.54 g·dl⁻¹, MW \approx 30,000; Trimethylphosphite (TMP): Aldrich Chemical Co. (Milwaukee, Wisc.), P(OCH₃)₃ Aldrich technical grade, 97% dried over sodium at room temperature; 1,1,2,2-tetrachloroethane (TCIE): Aldrich Chemical Co. (Milwaukee, Wisc.), Aldrich technical grade; *p*-Dioxane: Aldrich Chemical Co. (Milwaukee, Wisc.), Aldrich 99+% spectrophotometric grade, dried over sodium at room temperature. Bromine: Fisher Scientific Co. (Pittsburgh, Pa.), Reagent A.C.S.; Cellulose acetate: Eastman Kodak Co. (Rochester, N.Y.), Acetyl content 39.4%; ASTM viscosity 45; Dichlorine 2: Sears Roebuck & Company, Commercial chlorinating agent, active

ingredient: sodium dichloro-S-triazinetriene dihydrate 100% (56% chlorine available).

Synthesis: Bromination and Phosphonylation of PPO

Bromination

Bromination of the phenyl ring of the PPO is achieved by adding (drop-wise at room temperature) 1.0 mol equivalent of bromine to 10 wt-% PPO predissolved in tetrachloroethane (TCIE). The ring bromination is carried out in the dark to avoid radical bromination of the methyl groups. When bromination is complete, the reaction vessel is exposed to light and the mixture is heated to reflux. A stoichiometric amount of bromine is added drop-wise to this refluxing mixture to obtain various percentages of bromination on the two pendant methyl groups. The polymer is precipitated by adding methanol to the cold solution, redissolved with methylene chloride, filtered, and reprecipitated with methanol. Detailed procedures are given elsewhere.⁷

Phosphonylation

Various batches of the brominated PPO were phosphonylated by adding the brominated PPO to the refluxing mixture of dioxane and trimethylphosphite (TMP).

Example: To a refluxing mixture of 100-ml TMP in 500-ml *p*-dioxane, 40 g of PPOBr in 500-ml *p*-dioxane is added slowly. The addition is completed within 2 hr. Refluxing is continued for another hour, until the solution becomes clear. The mixture is cooled to room temperature. The polymer (PPOBrP) is precipitated in hexane, redissolved in *p*-dioxane, filtered through Celite, reprecipitated in hexane, and dried in vacuum. The bromophosphonated polymer is obtained with 90% yield. Selected results are shown in Table I.

Membrane Preparation

Polyphosphonates and cellulose acetate can be dissolved in a mutual solvent (e.g., dioxane) to produce a clear solution from which a dense, homogeneous film can be cast. The casting of an asymmetric alloy membrane made of polyphosphonate and cellulose acetate frequently requires a composite solvent mixture, e.g., methanol/acetone/formamide (41/41/18 w/w/w). In such cases, the nature of the polymers often dictates that each polymer be dissolved separately in a different solvent; the two polymer solutions are then mixed to give a clear, homogeneous solution ready for casting. This aspect is discussed in detail in the following sections.

Casting of a Dense Alloy Film

A 7-in. strip of 10–15 wt-% polymer solution is evenly poured across one end of a 10 × 22-in.² glass plate. A casting knife (doctor blade), preset to give the desired thickness, is drawn at an even rate down the entire length of the plate. The cast solution is placed in a dust-free hood and allowed to dry at room temperature. When the layer is completely dry (after a period of 12 to 24 hr), the

TABLE I
Analysis of Brominated and Phosphonylated PPO

Structural formula	Designation	Elemental Analysis		NMR Analysis			
		% Bromine	Bromine per unit	No. Bromine ϕ -Br	No. Bromine $-\text{CH}_2\text{Br}$	No. Phosphorous P-OCH ₃	No. Methyl ϕ -CH ₃
<p>CH₃ CH₂Br(0.50)</p>	PPOBr (0.50)	50.69	1.49	≈1.00	0.63	0.00	1.40
<p>CH₃ CH₂Br(0.75)</p>	PPOBr (0.75)	52.34	1.59	≈1.07	0.80	0.00	1.00
<p>CH₃ CH₂Br</p>	PPOBr	59.38	2.12	≈1.00	1.23	0.00	0.74
<p>CH₃Br CH₂Br</p>	PPOBr ₂	64.82	2.77	≈1.00	1.67	0.00	0.22
<p>CH₃ O ↑ CH₃-P-OCH₃</p>	PPOBrP	25.22	0.944	≈1.00	0.00	≈1.00	≈1.00

glass plate is immersed in a deionized water bath. The dense film is subsequently released from the surface to give a clear, transparent alloy which displays a single glass transition temperature T_g .^{6,7}

Casting of Asymmetric Membranes

Asymmetric membranes were cast in a glove box under a dry nitrogen atmosphere. The polymer solution was cast onto a glass plate or polyethylene release paper using a casting knife. The solution was left in the glove box under a nitrogen atmosphere for a 10- to 90-sec evaporation period. Subsequently, the plate with the polymer solution on its surface was quenched by submerging in a deionized water bath at 1°C. The membranes were stored in deionized water.

Annealing

Dense and asymmetric membranes were annealed in deionized water at 80–95°C.

Testing for Desalination of Water

The membranes were tested in a high-pressure reverse osmosis rig equipped with round, stainless-steel cells, Berghof/America Inc. (Derry, N.H.). The membrane surface area was 38.4 cm², and the feed-flow rate was maintained within the range of 1–2 gpm. Salt rejection and flux rate were determined by

$$\text{SR}\% = 100 \left(1 - \frac{\text{concentration of permeant}}{\text{concentration of feed}} \right)$$

$$\text{Permeation rate} = \frac{\text{volume permeated}}{\text{time} \times \text{permeation area}} \left(\frac{\text{cm}^3}{\text{sec} \cdot \text{cm}^2} \right),$$

(or gal/ft² · day = gfd).

Feed Solution

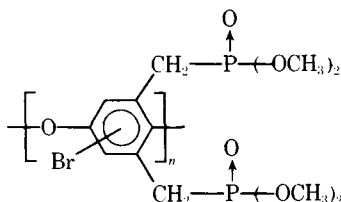
Membrane transport was measured with two saline water solutions: 10,000 ppm NaCl and 3000–6000 ppm Na₂SO₄. Some membranes were tested for chemical stability with respect to the presence of chlorine and oxidizing agents by adding 75–500 ppm sodium or calcium hypochlorite (or dichlorine 2) to the feed solutions. Free chlorine was maintained in the range of 20–100 ppm and was monitored by a free chlorine colorimetry test kit. The pH was usually maintained in the range of 4–7 and for some evaluations was raised to 10.7. This level was monitored by a pH meter.

RESULTS AND DISCUSSION

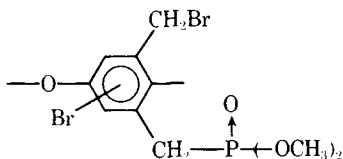
Dense Membranes

Five principal forms of the brominated polyphosphonate modification of PPO were prepared with the general polymer unit formulas:

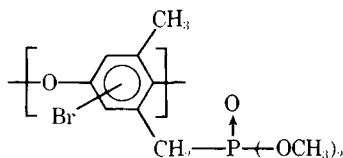
PPOBrP₂: both pendant methyl groups phosphonylated



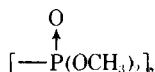
PPOBrP₂(Br): trace levels of CH₂Br left in the polymer chain as crosslinking moieties.



PPOBrP: one phosphonate ester group per polymer unit. PPOBrP (0.75): averaging three phosphonate ester groups per four polymer units. PPOBrP (0.05): averaging one phosphonate ester group per two polymer units.



The solubility range of these polyphosphonates is progressively increased with the degree of phosphonylation.¹⁰ The polymers designated PPOBrP and PPOBrP₂ are soluble in alcohols (e.g., methanol and butanol), in cyclic ethers such as THF and dioxane, and in chlorinated hydrocarbons; however, they are not soluble in acetone. The latter is a good solvent for cellulose acetate and is used as a major component for the fabrication of asymmetric membranes from this polymer. Dense isotropic alloy membranes were cast from a dioxane solution of the polyphosphonates (PPN) and cellulose acetate. The transparent film cast from this solvent displayed a single glass transition temperature ranging between 163–190°C. The water absorption of this alloy as a function of PPN weight fraction in the membrane is shown in Figure 1. As anticipated, PPOBrP₂, due to the abundance of pendant hydrophilic phosphonyl ester groups



exhibits a higher degree of water absorption than does PPOBrP.

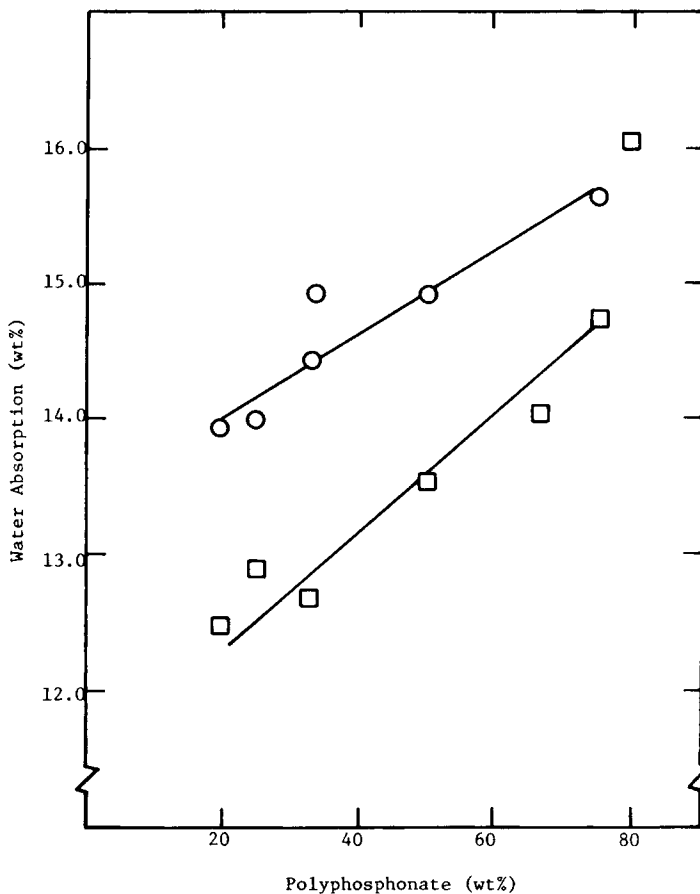


Fig. 1. Water content vs polyphosphonate fraction in a water equilibrated alloy membrane (21°C). (○) CA/PPOBrP₂; (□) CA/PPOBrP.

According to calculations from the theory of diffusive permeability of saline (NaCl) water through noncharged membranes,¹¹⁻¹³ reverse osmosis membranes, which display water content in the range shown in Figure 1, might exhibit maximum salt rejection in the range of 93%–96%. However, polymers with similar water content can differ greatly in clustering characteristics, especially due to microphase separation (between amorphous and semicrystalline regions) and the existence of hydrophilic domains in the matrix. As a result, transport properties can differ markedly.

Dense alloy membranes of CA/PPOBrP₂ were tested in the reverse osmosis rig with a feed solution of 10,000 ppm NaCl. Nonannealed membranes, in the as-cast state, often yield salt rejections of less than 50%. Annealing drastically improves the separation properties of the membranes, and salt rejections exceeding 90% were obtained. These results conform with previous reports that annealing substantially improves permselectivity for the separation of organic liquid mixtures by polyphosphonate/cellulose ester alloy membranes.² The response of the alloy membrane to annealing also corresponds to the observation of Manjikian¹⁴ for cellulose acetate membranes.

The correlation between the annealing temperature and membrane performance was evaluated for the composition CA/PPOBrP₂ (1/1 w/w) (Fig. 2). This dense alloy membrane was cast from a 15 wt-% solution in dioxane. The dry film (6.66 μm thick) was cut into samples which were annealed at different temperatures and then tested in the reverse osmosis rig. A temperature of 90–95°C was found to be optimum for enhancing membrane separation capability. This temperature range was found to be adequate for annealing the asymmetric alloy membranes cast from the same polymer composition ratio, as shown below.

The performance of the various membranes, as a function of the alloy composition, was also directly determined in reverse osmosis tests. Results are shown in Figure 3. It is most significant that there is no trade-off between separation and flux. The best membrane, CA/PPOBrP₂ (1/1 w/w), yielded the highest salt rejection and the best flux rate. This is probably due to an intermolecular rearrangement within the polymer alloy. The water absorption curves in Figure 1 do not, according to simplified transport theory, predict such behavior. How-

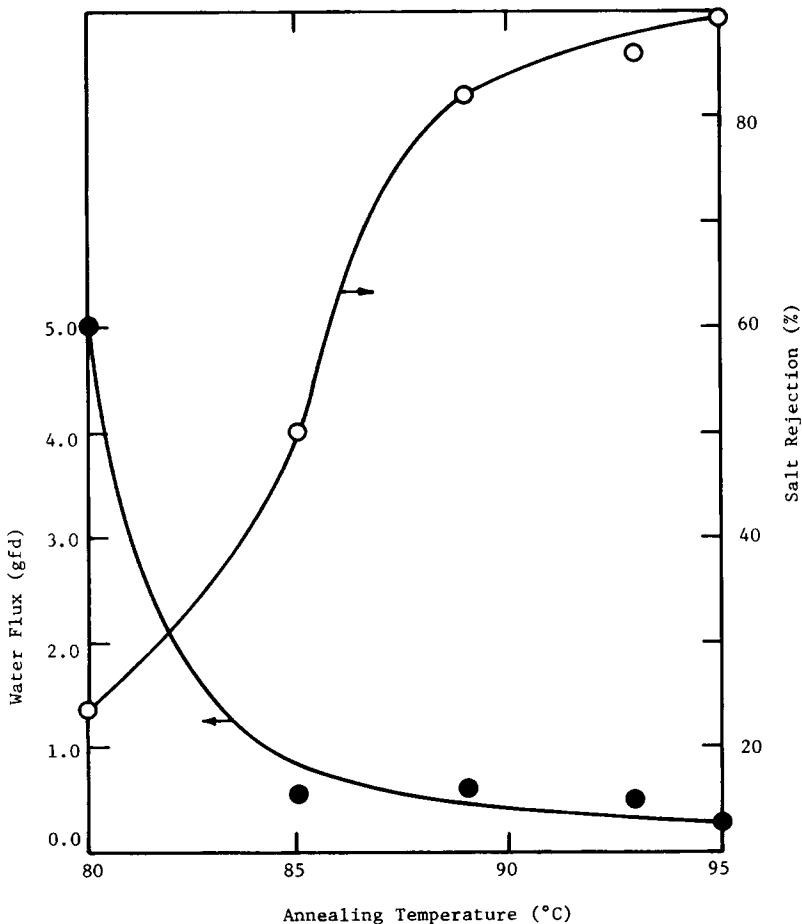


Fig. 2. Flux and salt rejection vs annealing temperature for dense alloy membrane CA/PPOBrP₂ (1/1 w/w) cast from dioxane (6.66 μm). Feed solution = 10,000 ppm NaCl. Hydraulic pressure = 800 psi.

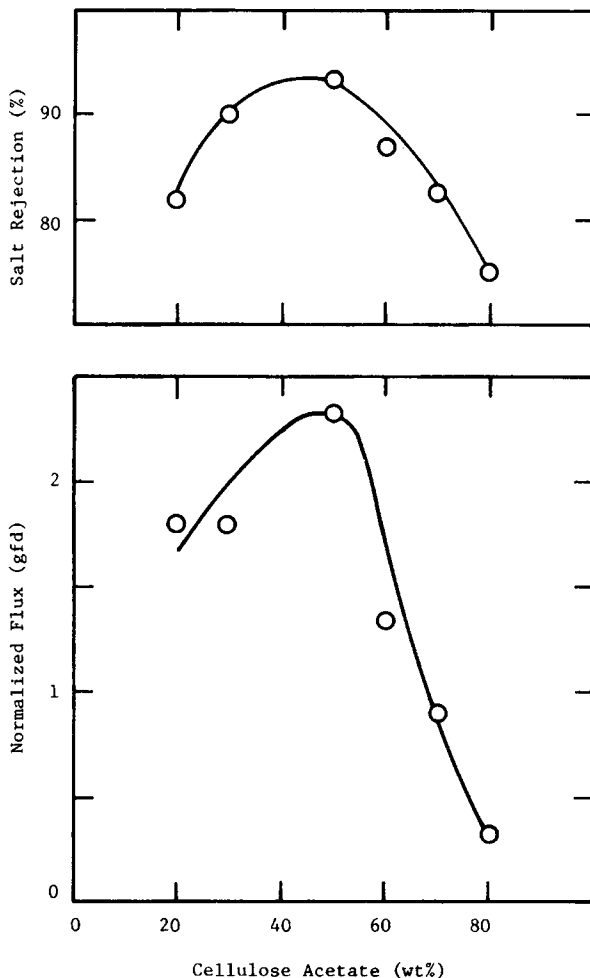


Fig. 3. Flux and salt rejection vs cellulose acetate fraction in a dense alloy membrane composed of CA/PPOBrP₂. (Dense membranes with a thickness of 7–18 μm were annealed in water at 90°C and tested at 800 psi with 10,000 ppm NaCl feed solution. The flux rate was normalized for a membrane thickness of 1 μm .)

ever, some indication that such a rearrangement does occur has been shown previously¹⁰ (when a series of polyphosphonate/cellulose acetate alloys with a weight ratio greater than 1 were exposed to a polyphosphonate solvent. The PPN leached out from the alloys until a stable, 1/1 ratio was reached).

Asymmetric Alloy Membranes

The formulation of a solvent system which would provide a membrane with an anisotropic morphology, consisting of a dense skin resting on a porous layer, is dependent on interactions between the polymer, solvents, and quenching liquid. Solvent selection was based on the method of Klein and Smith,¹⁵ which utilizes Hansen's solubility parameter diagrams. These investigators assumed that the solubility parameter of a solvent mixture is an additive function of the component parameters. Thus,

$$\delta_t^2 = f_1\delta_1^2 + f_2\delta_2^2 + f_3\delta_3^2 + \dots + f_n\delta_n^2 \quad (1)$$

where f is the volume fraction of each component, δ is the solubility parameter of each component, and δ_t is the resultant solubility parameter of the solvent system.

While the above assumption [eq. (1)] is difficult to justify when judged by stringent thermodynamic criteria, it has proved to be very useful when dealing practically with polymer systems. In practice, one can employ Hansen's solubility parameters,¹⁶ which relates to δ (Hildebrand) by the following expression:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

The fractional parameters reflect the dispersion, polar, and hydrogen interactions of δ . Every organic molecule can be characterized by δ , δ_d , δ_p , and δ_h values. Figure 4 illustrates the solubility parameter diagrams of PPOBrP₂ and cellulose acetate. The encircled areas encompass all organic compounds that are solvents for the designated polymers; every organic solvent is represented as a point on the δ_p , δ_h plane according to its solubility parameter value. The solubility parameter areas of the polymers do not provide a single δ value¹⁰; rather, they provide a range of solvent-polymer interactions. The solubility parameters of the solvent mixture (δ_t) should be located within the solubility areas of the polymer components in the solubility diagram (Fig. 4).

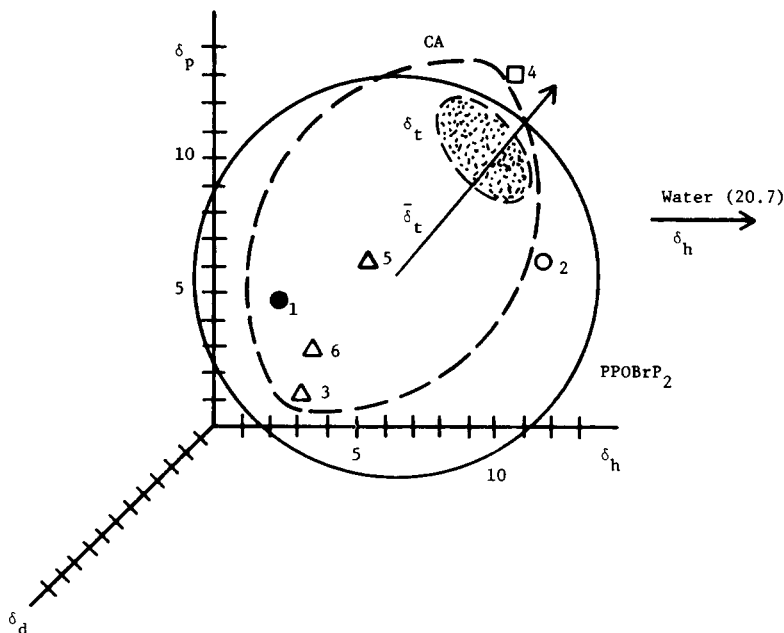


Fig. 4. Solubility parameter diagram showing PPOBrP₂ and cellulose acetate solubility areas and the locus of the organic solvents from which asymmetric membranes were cast. δ_t represents the desired location of the solvent combination as calculated from eq. (1). $\bar{\delta}_t$ is a hypothetical vector through which δ_t is progressively transferred out of the solubility area of the polymers upon quenching with water. (1) Acetone; (2) methanol; (3) dioxane; (4) formamide; (5) dimethyl formamide; (6) tetrahydrofuran. (●) CA-solvent; (○) PPOBrP₂-solvent; (Δ) CA/PPOBrP₂ mutual solvent; (□) Nonsolvent for both polymers.

From the literature which describes the formation of asymmetric membranes, Klein and Smith¹⁵ compiled working rules regarding the requirements of a casting solution:

1. The casting composition (δ_c) should be near the solubility boundary facing the quench medium.
2. A volatile solvent component should be such that its loss will move the composition out of the solubility area, rather than into it.
3. The solid's content at the solution boundary must be high in order to cause a rapid transition from solution to gel.
4. All components of the system should be miscible with the quench medium (nonsolvent).

Some exceptional casting compositions in which one of the solvent components is immiscible with the quench medium (water) were explored recently and are reported elsewhere.¹⁷

The mechanism of dense skin formation is still unclear; however, it is evident that the polymer concentration in the surface layer of the cast solution is progressively increased during the evaporation period and upon exposure to the quench solution. For some polymer/solvent systems, the evaporation period is not necessary, and an asymmetric structure is formed *in situ* upon quenching.¹⁸ However, when more than one polymer component is involved in a rapid gelation process, the interaction of the aqueous quench medium with the two polymer components might lead to a microphase separation. In fact, this characteristic has been successfully utilized in the spinning of anisotropic polysulfone hollow fibers with a highly porous skin.¹⁹ In this case, polysulfone/poly(vinylpyrrolidone) (3/2), a highly compatible polymer system, was spun and quenched from its DMF solution directly into water. The two polymers phase separated and the PVP domains dissolved into the quench solution, leaving a porous skin. In such a case, the pore dimensions of this skin can be manipulated by controlling the nature of phase separation.

An evaporation period was found to be mandatory for the formation of PPOBrP/CA asymmetric alloy membranes. This establishes a highly concentrated mixture of the polymeric components at the surface of the cast solution, which apparently leads to the formation of a homogeneous skin, as shown by scanning electron microscopy studies. For this reason, volatile solvent components were employed for the casting formulations. The solvent systems were selected empirically to fit the above rules. The resultant solubility parameter δ_c^2 of the mixture, as a first-order approximation, was computed to be located near the solubility boundaries shown in Figure 4. It should be emphasized that the physical meaning of δ_c^2 , as calculated from eq. (1), is dubious; however, it has been shown to be useful and correlates quite adequately when employed in membrane fabrication¹⁵ where the numerical value serves as a semiquantitative function in an arbitrary set of coordinates.

More than 30 solvent systems, including binary, ternary, and quaternary mixtures, were formulated for the fabrication of PPOBrP/CA asymmetric alloy membranes. Selected formulations and respective membrane performances are shown in Table II. The various polymer solutions result in numerous membranes with different characteristics; nonetheless, all can be compared by their water flux rates and salt rejections. Since many variables are involved in

TABLE II
Representative Casting Formulations and Related Performance of Asymmetric Alloy Membranes

	Formula index number															
	1	3	4	5	8	10	11	13	15	17	22	23	24	25	26	27
Solvents (wt-%)																
Acetone	23.0	23.1	21.6		40.0	44.6	33.3	37.5	33.3	20.1	32.3	26.5		24.5	44.5	
Dioxane	58.9	58.8	55.1	55.2				43.7				9.7				
DMF				24.8											29.7	29.7
Methanol					25.0	23.1	33.3		33.3		32.2	31.9	21.0	24.4		
Formamide					12.5	15.4	14.8		14.8	6.7	17.7	14.1	43.4	34.9		
THF										54.4			21.0			
Triethylamine																
			6.3													
Polymers (wt-%)																
CA-3 (Eastman)															4.0	4.0
CA-25 (Eastman)																
CA-45 (Eastman)	4.6	9.2	8.6	10.0	10.0	9.2	9.3	12.5	9.3	9.4	8.9	8.9	7.7	8.1	8.9	8.9
PPOBrP ₂				10.0	12.5	7.7					8.9			8.1	12.9	12.9
PPOBrP							9.3	6.3	9.3							
PPOBrP (0.75)	13.5	8.9	8.4							9.4						
PPOBrP (0.50)												8.9	6.9			
PPOBrP ₂ (Br)																
Casting conditions																
Casting thickness (mil)	6	5	5	7	7	8	10	10	10	10	10	7	7	7	7	10
Evaporation period (sec)	60	30	35	50	55	45	15	45	25	45	25	60	30	10	20	60
Results																
Flux (gfd) (800 psi)	9.3	10.6	10.6	2.7	3.9	0.9	17.0	0.6	11.0	1.2	8.1	3.4	12.8	12.5	7.1	24.0
Salt rejection (%) (10,000 ppm NaCl)	65	62	42	53	81	78	86	40	94	59	90	93	86	84	82	50

the casting of an asymmetric membrane (e.g., solvent composition, casting temperature and thickness, evaporation period, quenching temperature), experimental designs are needed for selecting the chief parameters for each alloy composition. However, this is beyond the scope of the present paper, and only a few prominent variables are discussed here. The best results were obtained from a composition of PPOBrP/CA cast according to formulas 11 and 15 in Table II. A characteristic performance is shown in Figures 5 and 6. The effect of the duration of the evaporation period on membrane transport properties is shown in Figure 7. For this specific casting formula, the optimum evaporation period ranged between 15 and 35 sec.

The morphologies of these membranes vary according to the casting formulations used. A unique morphology is shown in the scanning electron micro-

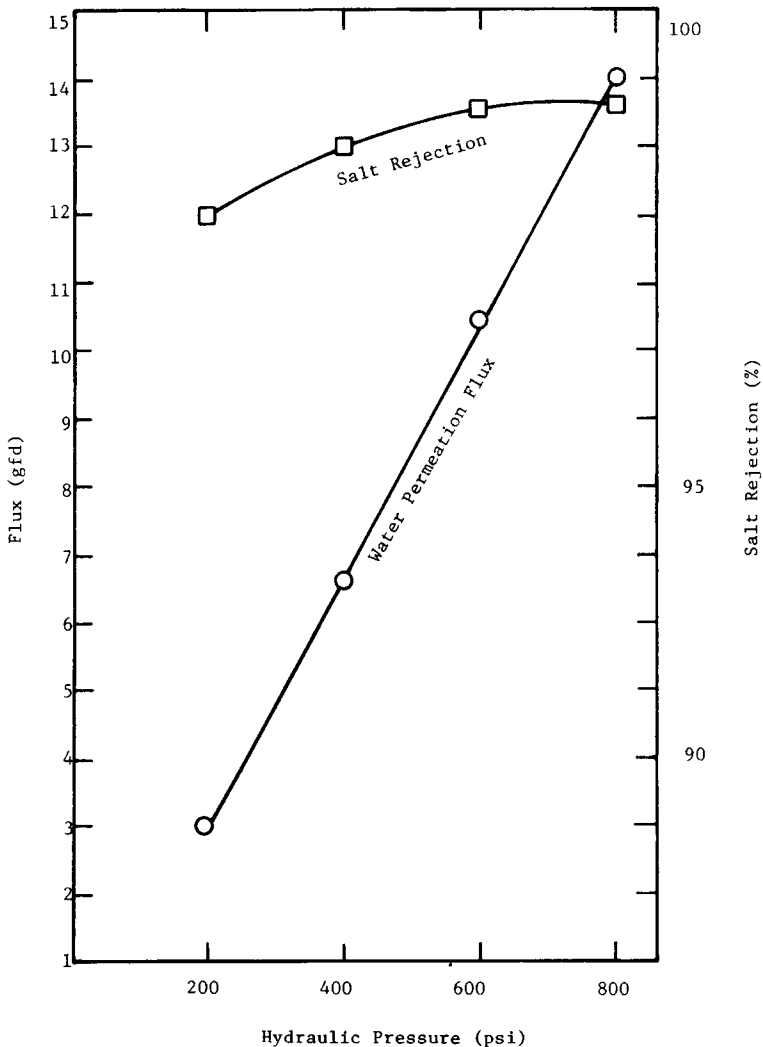


Fig. 5. Flux and salt rejection vs pressure obtained from asymmetric alloy membrane CA/PPOBrP (1/1 w/w) of the type cast from formula 11 (Table II). Feed solution = 10,000 ppm NaCl, 40 ppm Cl_2 . Annealing temperature = 94°C (25-sec evaporation period).

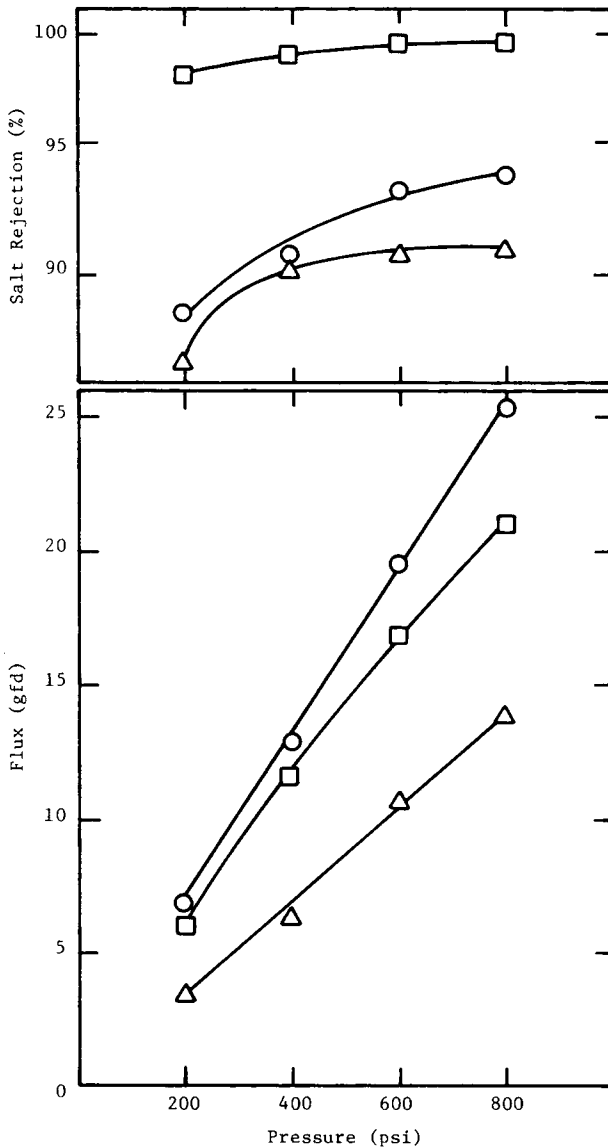


Fig. 6. Flux and salt rejection vs pressure for three different asymmetric alloy membranes of PPN/CA (1/1 w/w). No compaction was observed in 14-day testing period. Feed solution = 3000 ppm Na_2SO_4 , 20–80 ppm Cl_2 (~500 ppm NaOCl). Annealing temperature = 90–95°C.

graphs in Figures 8 and 9. A skin about $0.1 \mu\text{m}$ thick resting on a porous layer which displays a two-phase morphology is clearly seen. The spheres appear to be grown out of the polymer network (Fig. 8) and upon exposure to elevated hydraulic pressure split from the matrix into individual disconnected spheres. The density of the spheres appears to be higher than that of the matrix since they are hardly affected by the hydraulic pressure (> 1000 psi), while the continuous polymer network clearly shows evidence of compaction. Evidence of these dense spheres can also be detected through the porous down face of the membrane, as seen in Figure 9(c). The overall structure resembles that of composite ma-

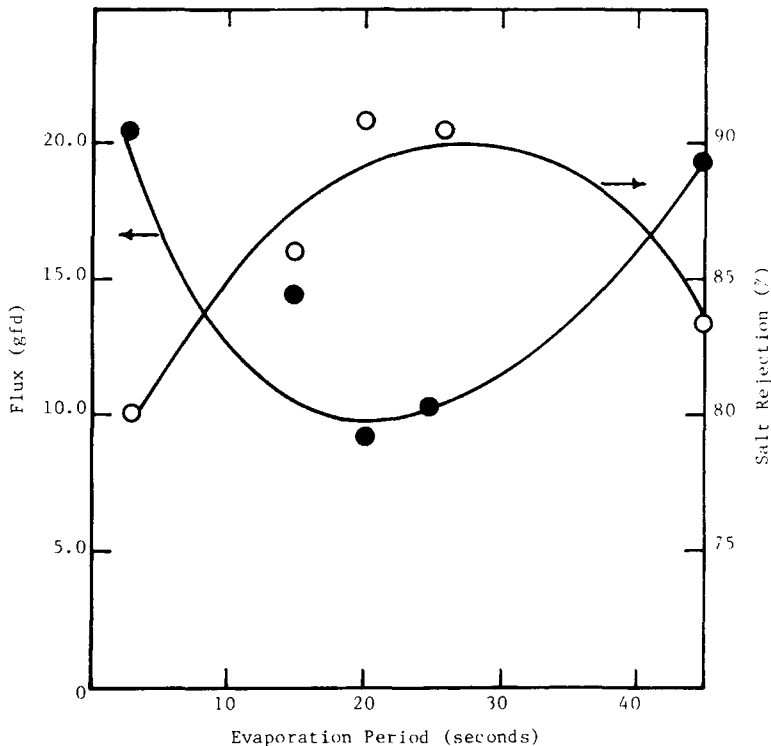


Fig. 7. Flux and salt rejection vs evaporation period for asymmetric membranes cast from CA/PPOBrP formula index 11 (Table II). Feed solution = 10,000 ppm NaCl. Hydraulic pressure = 800 psi. Annealing temperature = 90°C.

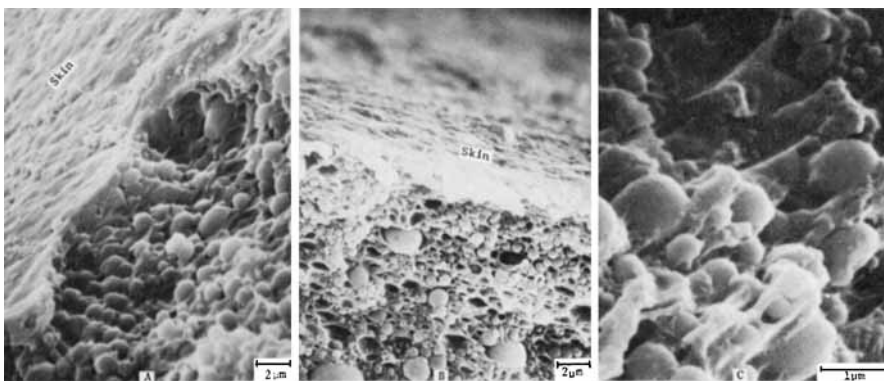


Fig. 8. Asymmetric alloy membranes cast from formula index 15 (Table II): (A) before testing, (B) after 14 days of testing under elevated pressure up to 1000 psi, (C) cross-section of untested membrane, in which the spheres appear to "grow" out of the matrix. These micrographs clearly indicate that physical separation of spheres is induced by the hydraulic pressure (B). Nevertheless, membrane performance does not deteriorate during 14 days of testing (see Figs. 5 and 6).

terials in which a rigid component is added to a soft continuous matrix for physical reinforcement. While the first assumption was that the cellulose acetate and the PPOBrP had phase separated, a rigorous scanning study for domains rich with bromine and phosphorus using a PGT-1000 x-ray analyzer gave no indication that microphase separation between the two polymer components

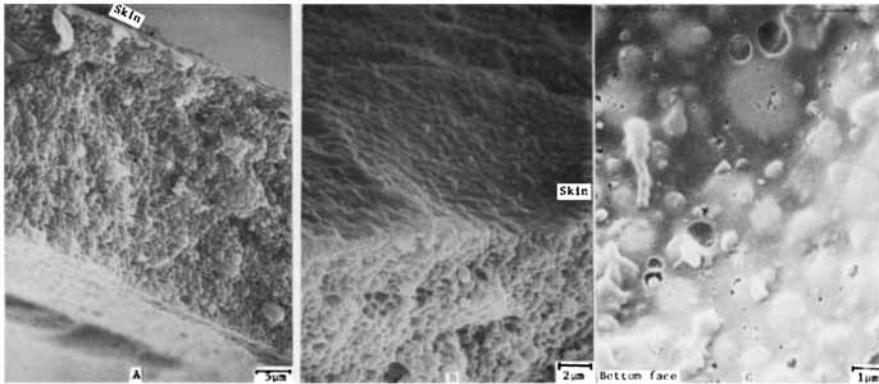


Fig. 9. Asymmetric alloy membranes cast according to formula index 15 (Table II). This membrane was tested for 14 days in a reverse osmosis rig and was exposed to hydraulic pressure up to 1000 psi. (A) Membrane cross section. The horizontal slits in the lower part of the membrane result from the initial compaction. (B) Membrane cross section showing a mounded dense skin, resulting from phase separation within the membrane which produces very dense spheres. (C) On the porous bottom face of the tested membrane, marks of the dense spheres can be clearly seen.

is what actually is seen in this micrograph. Therefore, the apparent phase separation shown in the cross section of Figures 8 and 9 is not separation of the two polymeric components. Rather, it is a separation of two phases with different PPOBrP/CA alloy ratios. Some other alloy membranes which were cast from different formulations display morphologies similar to those of conventional asymmetric cellulose acetate membranes, a skin resting on an open-celled foam, as shown in Figure 10. Further studies on the nature of the various morphologies will be reported elsewhere.

Employing formulations 11 and 15 (Table II), alloy membranes were characterized for hydraulic transport, water transport, and salt rejection. As shown in Figures 11 and 12, the degree of phosphonylation of the PPOBrP has a dramatic influence on the alloy membrane properties when cast from a fixed solvent

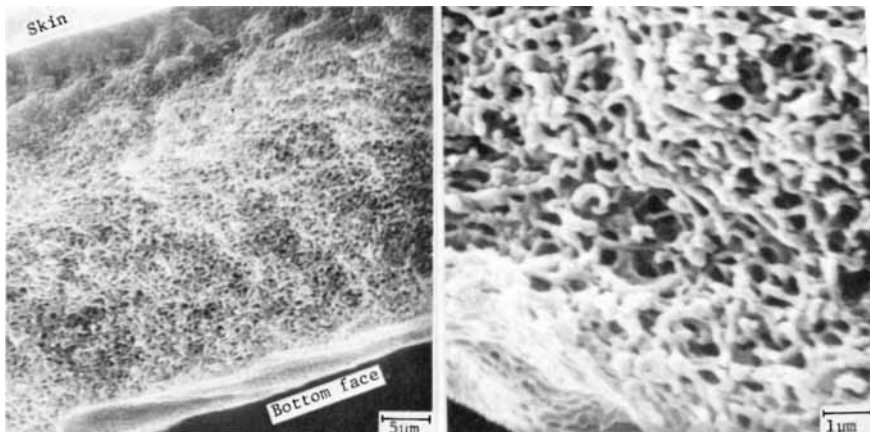


Fig. 10. Asymmetric alloy membrane cast according to formula index 26 (Table II). The morphology of this CA/PPOBrP (1/1 w/w) membrane resembles that of membranes cast from pure cellulose acetate, and displays a completely different structure from that shown in Figures 8 and 9. The membrane shown in the micrographs was tested under hydraulic pressure up to 1000 psi. No evidence of compaction in the open-celled foam structure can be seen.

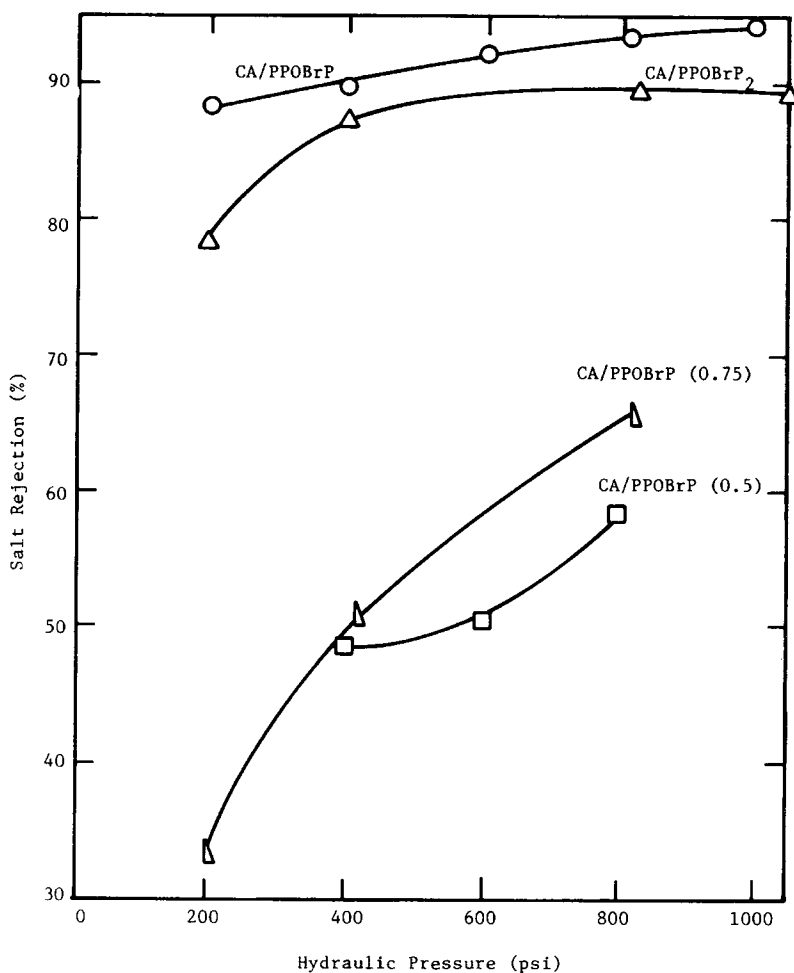


Fig. 11. Salt rejection vs hydraulic pressure of four alloy membranes cast from formula index 11 (Table II) with different polyphosphonate components.

system (i.e., acetone/methanol/formamide 33.3/33.3/14.8 by weight). Such behavior is expected since various alloy combinations, both in solution and as dense solid phases, display different physical and chemical properties. Thus, the results delineated in Figures 11 and 12 do not necessarily indicate that PPOBrP(0.50)/CA is in general an inferior alloy combination since optimum solvent requirements for each blend are different.

The chemical and mechanical stability of these membranes was also tested. Chemical deterioration of reverse osmosis membranes is caused mainly by pH variation and oxidation. Large pH variation of saline feed water would cause a fast degradation and hydrolysis of the polymeric membrane, e.g., cellulose acetate undergoes hydrolysis²⁰ above and below the range of pH = 4.5–7.2. Oxidative ingredients are usually incorporated into water that is subjected to a purification or desalination process, often in the pretreatment stage. In most cases, this treatment is accomplished through chlorination of the water to the level of 1–2 ppm. Most reverse osmosis membranes have low tolerance to

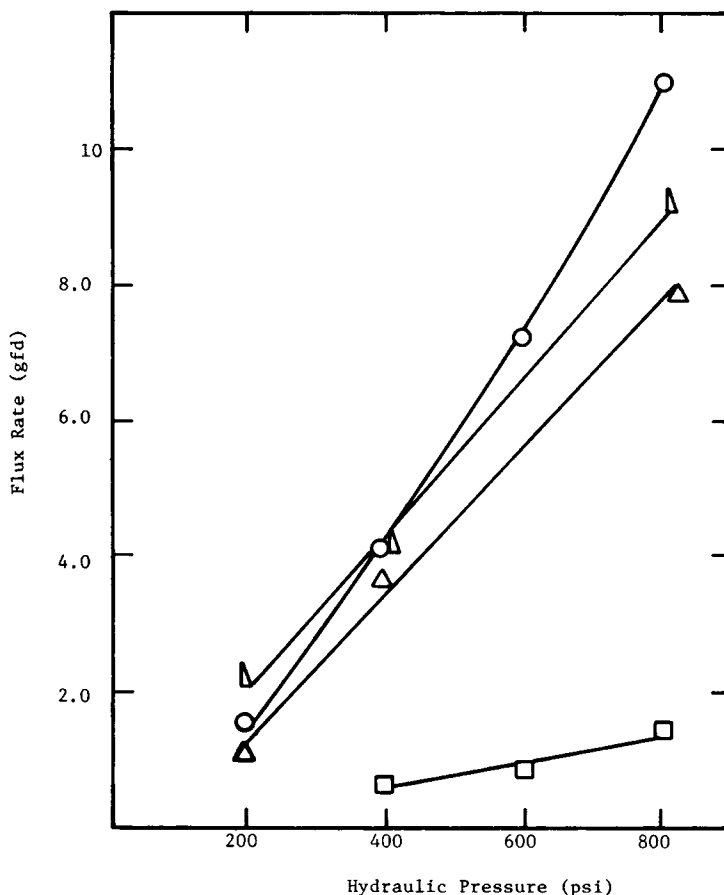


Fig. 12. Flux rate vs hydraulic pressure of the four alloy membranes shown in Figure 11. (○) CA/PPOBrP, (△) CA/PPOBrP (0.75), (▽) CA/PPOBrP₂, (□) CA/PPOBrP₂ (0.5).

chlorine, and sometimes deterioration occurs within a matter of hours, as is the case with asymmetric polyamide and some composite membranes [PA-300 and NS-100, based on poly(ether amide) and polyurea, respectively].

The CA/PPOBrP alloy membranes were tested for short-time durability under a relatively high pH (10.4–10.7) and feed water overdosed with chlorine (20–80 ppm). Selected results are presented in Figures 5, 6, and 13. While there is no significant change in the salt separation, there is often a clear improvement in the flux rate, as shown in Figure 13. The rationale for the selection of the poly(bromophenylene oxide phosphonate), PPOBrP, over the nonbromo derivatives (PPOP) as a component in the alloy, was that the latter is vulnerable to electrophilic substitution in positions 3 and 5 of the phenyl ring. The pre-bromination of the phenyl ring was also shown to protect the aromatic ether link.⁷ The large bromine atom shields the phenylene oxide links, thus preventing electrophilic and radical attack and chain degradation. The remarkable tolerance of the alloy membranes to the overdosed chlorine in the saline solution seems to support this approach. The performance of this membrane in a high pH environment is also notable. The saponification of cellulose acetate is enhanced

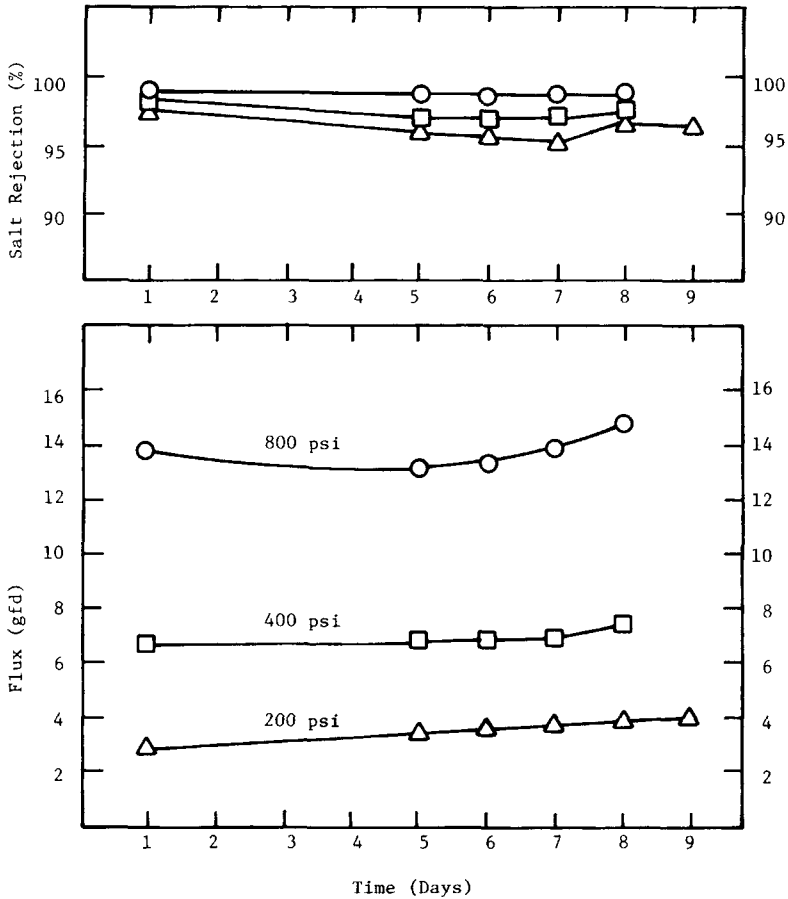


Fig. 13. Flux and salt rejection vs time for asymmetric alloy membrane (CA/PPOBrP 1/1 w/w) shown in Figure 8. Feed solution = 400–4500 ppm Na_2SO_4 , 20–80 ppm Cl_2 . pH = 10.4–10.7.

by the presence of hydroxyl groups on the cellulosic unit; however, the specific interaction of the acetyl/hydroxyl couples with the phosphoryl groups of the polyphosphonates seems to decrease their accessibility to alkaline hydrolysis, which becomes sterically hindered. This hypothesis is currently under study.

As for the mechanical durability, scanning electron micrographs of the tested membrane clearly indicate the occurrence of compaction in some networks [Fig. 9(a)]. Most reverse osmosis membranes experience a continuous decrease in hydraulic permeability as a result of membrane compaction. Nevertheless, the matrix compaction shown in Figure 9(a) is attributed to the initial response of these membranes to the elevated hydraulic pressure. This probably occurs almost instantaneously with the exposure to pressure, since hydraulic permeability measurements taken within the first 8 hr of a reverse osmosis run, employing a hydraulic pressure of 800 psi, already exhibited a positive slope (Fig. 14). For most formulations tested (Table II) the collapse pressure for the membranes is far above 1200 psi.

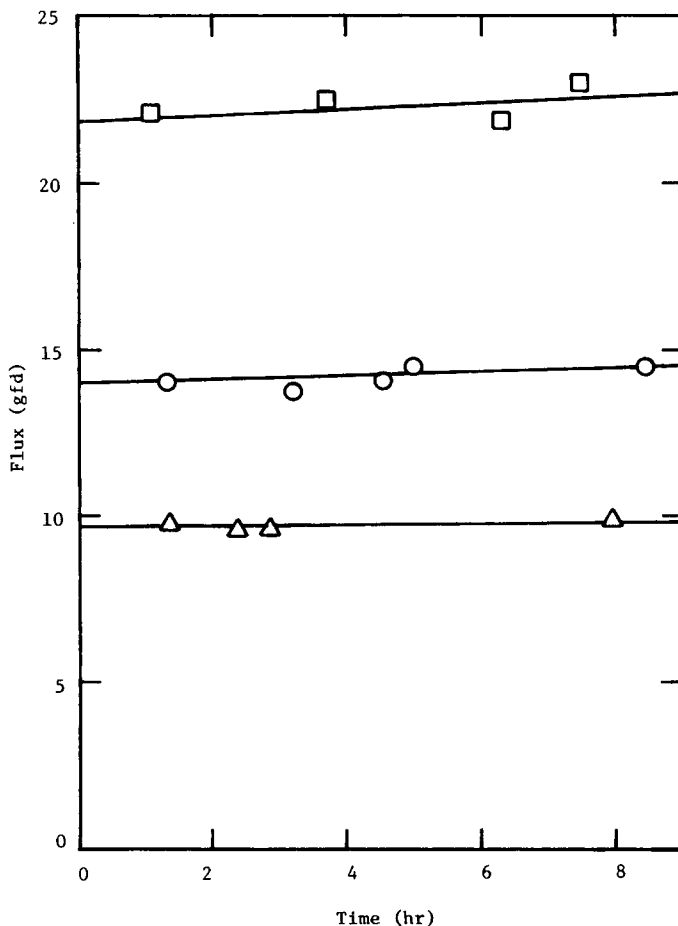
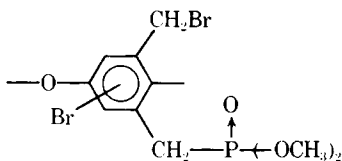


Fig. 14. Initial slope of flux vs time for asymmetric alloy membrane (CA/PPOBrP 1/1 w/w). Feed solution = 3000 ppm Na_2SO_4 . Hydraulic pressure: Δ = 200 psi, \circ = 400 psi, \square = 800 psi.

Crosslinked Alloy Membranes

A chemical crosslink between the two polymeric components in the membrane can be achieved by retaining some of the bromomethylated group.⁶ A molecular unit such as



would react with the cellulose acetate primary hydroxyl group, either upon annealing or spontaneously (but slowly) upon exposure to visible light. This crosslinked alloy is nonsoluble. Two asymmetric membranes of this type are shown in Table II (formulas 23 and 24). Preliminary results indicate that such membranes are more stable chemically than conventional alloys, and a study of such membranes is in progress.

CONCLUSIONS

This study is the first of its kind in which two such dissimilar polymer chains—cellulosic and aromatic ether—have been compounded successfully to give an asymmetric semipermeable membrane for high-pressure reverse osmosis. There are numerous parameters and many polymer combinations that have not yet been studied. To make a significant increase in the salt separation capabilities of the cellulose acetate/poly(bromophenylene oxide phosphonate) alloy membranes, the water absorption of these membranes has to be less than that reported in Figure 1 (apparently less than 12 wt-%). This can be achieved by dismantling the residual alcohol groups in the cellulose acetate component by further crosslinking the alloy components, and by deriving the proper casting formulation and obtaining better membranes with PPOBrP(0.75 or 0.5), which contains fewer hydrophilic moieties. These aspects are being studied simultaneously with the effort to substitute other polymers for the cellulose. The results will be reported in a subsequent paper.

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