Preparation and Structure of Cross-Linked Asymmetric Membranes Based on Polystyrene and Divinylbenzene

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SYNOPSIS

Asymmetric polystyrene-based membranes were prepared by photocross-linking with divinylbenzene (DVB) combined with phase-inversion steps. The primary variables examined were original polystyrene concentration in the membrane casting solution and degree of cross-linking. The effects of these upon membrane morphology and reverse osmosis performance were determined. At higher DVB concentration, skin was formed at the top due to phase separation and at the bottom due to preferential polymer absorption at the support interface. An attempt was made to increase membrane ductility by incorporating low levels of liquid polybutadiene or styrene–butadiene block copolymer, but no significant change was measured. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Membranes are used for a range of applications, such as desalination, the treatment of industrial effluents, the synthesis of pure ionic compounds, and gas separations. The applicability of membrane technology depends upon the availability of high-performance membranes tailored for each specific purpose. As the range of applications expands, improved, cheap membranes with enhanced chemical stability and active life are sought.

Early artificial membranes were based on natural polymers such as cellulose. Since Reid and Breton[1] developed cellulose acetate for desalination membranes, there has been considerable activity in the field of reverse osmosis. Their discovery, along with the subsequent dramatic improvements in flux demonstrated by Loeb and Sourirajan,[2] has stimulated independent interest in reverse osmosis as an economic process in the desalination of brackish and sea waters.

However, it was found that cellulosic membranes typically exhibit flux decline and have a limited resistance to chemical and biological attack. For example, cellulose acetate membranes are easily degraded at pH's greater than 6.5 due to acetyl group hydrolysis.[3] Long-term service temperatures are restricted to 40°C due to oxidation, and these membranes have also shown "pore compaction" after prolonged exposure to high pressure.[4]

Because of these limitations, new types of membranes from other synthetic polymers has been extensively investigated.[5-7] One solution is to provide a highly porous support and a very thin continuous top layer or "skin." The former allows high flux and adequate mechanical stability, whereas the latter bestows the salt-rejection properties required from reverse osmosis membranes. Early "composite membranes" of this type were described by Cadotte and co-workers[8] and comprised a polysulfone support with a toluene diisocyanate cross-linked polyethylene–imine skin. In principle, a range of materials can be selected for both support and skin, and disadvantages including biodegradability and compaction can be reduced. However, other properties including mechanical strength still need improvement.

These limitations were addressed by Fujita and Soane[9] who prepared asymmetric polystyrene (PS) membranes cross-linked with divinylbenzene (DVB). The casting solution comprised preexisting PS, styrene monomer, DVB, a photoinitiator system, and

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solvent. The mixture undergoes a UV-initiated first step in which some of the monomers partially polymerize and cross-link, followed by phase-inversion in one of several nonsolvents. The semistable porous mixture is exposed to UV light again, leading to a stable, cross-linked microporous network, as reflected by structure retention after swelling in carbon tetrachloride. The PS content is important, as is solvent composition. The former behaves as a poor solvent, assisting in the precipitation of newly formed polymer. Regardless of duration of preexposure time and nonsolvent composition, a 25% w/w PS content in the casting solution always led to the formation of a dense skin at the glass support interface, yielding products suitable for reverse osmosis. It was claimed that skin forms, due to preferential polymer adsorption at the glass interface, rather than by a coagulation/phase separation mechanism.

Kesting outlined membrane-forming routes under the classification of "phase inversion."[10] Of these, that by which skin-type asymmetric membranes are prepared by precipitation may be viewed as a subsidiary case, but, in fact, a number of methods have been studied in detail. For example, preferential evaporation of solvent from a solvent–nonsolvent–polymer mixture causing controlled polymer precipitation has been reported.[11-13] Alternatively, nonsolvent vapor can be imbibed into a polymer solution[14] and this concept is exploited commercially. Cooling of casting solutions can cause precipitation ("thermal gelation"). When this process is modified ("thermal inversion"), asymmetric membranes can be prepared.[15]

Membrane porosity not only depends upon polymer concentration in the casting solution, but also on the relative rates of solvent egress and nonsolvent ingress.[16] When ingress is much faster than egress (i.e., a high precipitation rate), highly porous membranes are formed; for aromatic polyamides, Strathmann[17] formed asymmetric skin membranes with fingerlike pores, having low salt rejection but high water flux. Low precipitation rates lead to dense sponges with low flux but high salt-rejection properties.

Porous PS/DVB copolymers have been intensively studied,[18-21] but although the mechanism of formation and structure–property relationships are now well known, tailoring to specific applications still requires significant effort.[20,21] Even when cross-linker density is high, pores can collapse during drying, and deterioration may occur in some solvents.[22-24] The rate of drying below the dry copolymer T_g also affects ultimate porosity.[22] Synthetic variables that control segmental mobility are thus important.

Ion-exchange and size exclusion chromatography resins are typically based on cross-linked PS/DVB copolymers. In this area as well, the role of synthetic variables upon pore structure has been studied.[25,26] Different copolymers are formed, depending whether a solvating diluent, such as toluene, or nonsolvating diluent, such as *n*-heptane, is added to the polymerizing mixture. Linear polymers including PS have also been incorporated at the beginning of copolymerization. Mixed diluents also lead to different matrix polymers; porous copolymer morphology varies widely, depending upon the chemical structure of the diluent.

Pore distribution and size is also governed by polymer–solvent interactions prevailing during and at the end of copolymerization. The swelling behavior of porous PS-*co*-DVB resins has been studied in good and poor solvents,[27-29] with nonsolvents being shown to shrink the network below V_f, the undiluted, unswollen polymer volume. Some fine-tuning of solvent solubility parameter can be achieved by using binary solvent–nonsolvent mixtures, so that the difference from the solubility parameter of the polymer is regulated and leads to the desired pore structure.

In this work, we prepared cross-linked asymmetric PS/DVB membranes based upon the formulations first outlined by Fujita and Soane.[9] In particular, we kept to their recommended PS concentration (25%) but varied DVB, as cross-link density is expected to strongly influence membrane morphology and reverse osmosis performance.[30] Small amounts of liquid polybutadiene or styrene–butadiene block copolymer were also added to the PS in the casting solution to determine whether they might affect structure or improve properties.

EXPERIMENTAL

Materials Preparation

In this work, we synthesized cross-linked membranes from a solution having an initial PS ("dead polymer") content of 25%. The DVB initial concentrations were 2, 5, 10, and 20% wt/wt, as it is known that the degree of cross-linking affects the pore size and morphology of the copolymer.[30] Attempts to overcome membrane brittleness by incorporation of either styrene–butadiene (SB) rubber or liquid polybutadiene (PBD) were made.

Four casting solutions were prepared with 25% PS, together with varying amounts of DVB. Samples coded S1–S4 in Table I contained 2, 5, 10, and 20% DVB (relative to total weight of casting solution), and the levels of styrene monomer and *N*-methyl 2-pyrrolidone (NMP) were accordingly reduced but at a fixed ratio of 1.75:1. Thus, at complete monomer conversion, the DVB content ratio for S1 would be 2.7 and 25% for S4. The remaining two solutions (S5 and S6) also contain 25% "dead polymer," with the elastomer being slightly more than 10% of the dead PS.

The PS (Chemplex, Melbourne) used has an M_n of about 260,000. DVB (Polysciences, 55–60% active) and styrene monomer (Ajax) were treated with "Drierite" to remove *p-tert*-butylcatechol inhibitor. The SB copolymer (Solprene 1205, Phillips Chemical Co.) used was a diblock containing 25 wt % styrene and with an M_n of 83,000. The liquid PBD (Polysciences) used has an M_n of 1000 and is about 85% 1,2 polymerized. The level of addition of these two elastomers is about 4% relative to the final, total polymer and so is somewhat lower than the 10% typically used to toughen polystyrene.[31]

Casting solutions containing the above components, together with benzoin photoinitiator and NMP diluent, were stirred in darkness for 24 h and vacuum-filtered through a glass sinter to remove insoluble matter and reduce bubbles. Each solution was spread onto a glass plate surrounded by a square 75 μm-thick PTFE gasket, to give a liquid film 5 × 5 cm. This was then supported within a Petri dish over a diluent reservoir, to reduce evaporation, as described by Fujita and Soane[9] (Fig. 1).

The film was exposed for 24 h to two 20-watt mercury vapor lamps (Sankyo Denki, GL 20SE) located 7 cm away, to form a partially cross-linked sol. The partially formed films were then coagulated in methanol nonsolvent, also containing benzoin. Finally, the nonsolvent side of the film was subjected to another 24 h UV exposure to give membranes that were rinsed and stored in water at room temperature.

Mechanical Testing

The tensile strengths and elongations at break of wet membranes were measured according to ASTM method D 882-79[32] with an Instron Model 1115 universal testing machine. A crosshead speed of 0.5 cm/min was used, and 2 × 5 cm dumbbells were tested in flat-faced grips set initially 2 cm apart. It is recognized that only nominal values are obtained, these being unadjusted to compensate for variations in bulk density.

Electron Microscopy

Membranes were dried in vacuum at 30°C for at least 1 week and fractured in liquid nitrogen prior to viewing by SEM. Jeol XA840 and Cambridge 360 instruments were used. A "Polaron" sputter coater was used to coat the samples with gold–palladium.

Reverse Osmosis Performance

For performance testing of cross-linked membranes at room temperature, a small static reverse osmosis cell developed by Kopecek and Sourirajan[33] was used.

RESULTS AND DISCUSSION

Introduction

The study of morphology can be broken up into three parts: First, the effect of DVB concentration was examined using fixed, optimized PS concentration. It should be noted, however, that while initial polymer concentration is fixed, polymer concentration after the first UV exposure in NMP/unreacted monomers will vary from S1 to S4.

Thus, other variations will be encountered beyond the initial DVB concentration. Hence, during stages

Table I Composition of Casting Solutions

Sample Code	DVB	PS	Styrene	NMP	Benzoin	SB Rubber	Liquid PBD
S1	2%	25%	46.1%	26.4%	0.5%	—	—
S2	5%	25%	44.2%	25.3%	0.5%	—	—
S3	10%	25%	41.0%	23.5%	0.5%	—	—
S4	20%	25%	35.0%	19.5%	0.5%	—	—
S5	10%	22.5%	41.0%	23.5%	0.5%	2.5%	—
S6	10%	22.5%	41.0%	23.5%	0.5%	—	2.5%

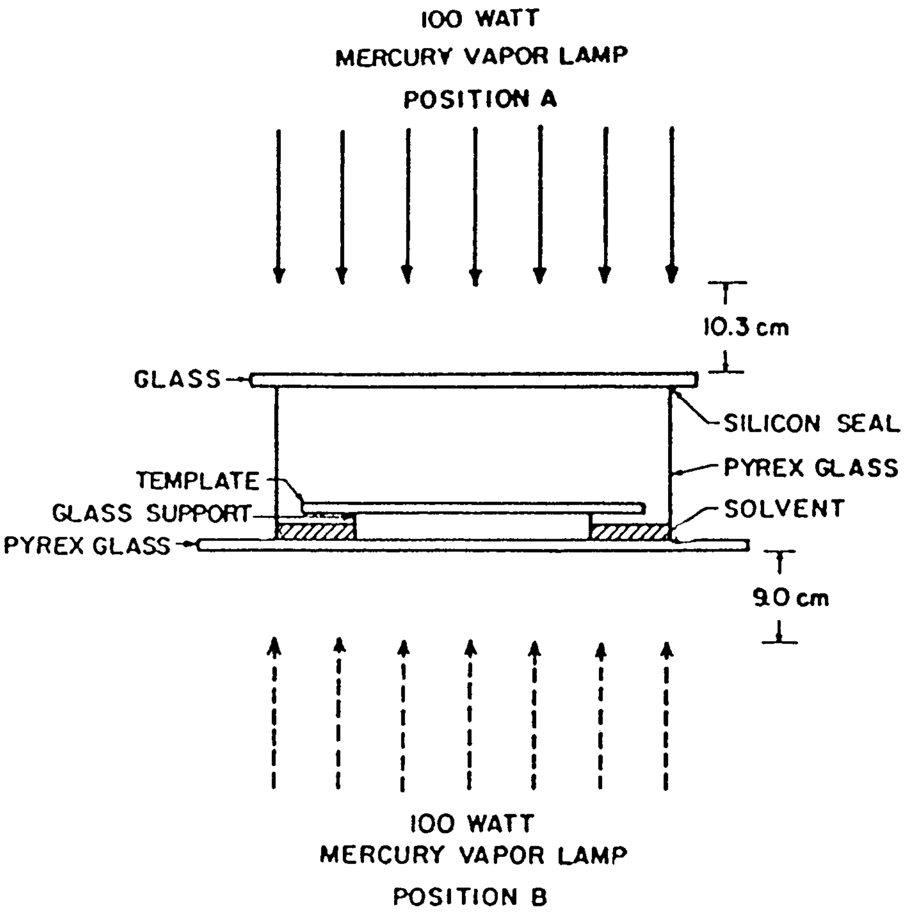

Figure 1 Experimental setup (9).

3-5 of the Fujita and Soane[9] model, intermediate polymer concentration will change, as will molecular weight. Such changes are unavoidable and important but not rigorously measurable.

The second part explores the influence of initial PS content upon final membrane structure. Very high and very low polystyrene concentrations give membranes without the thin skin needed for reverse osmosis. The third section deals with preliminary attempts to modify mechanical behavior by addition of low levels of elastomers into the membrane casting mixture.

Effect of DVB Content upon Skin Formation and Cross-sectional Morphology

Changes in microstructure with increasing cross-linking level are summarized in Figures 2-4. Figure 2 shows the cross section of each of the four membranes, S1-S4, where the primary variable is increasing DVB concentration. Figure 3 illustrates the top surface (i.e., air/solution interface) and bottom surface (i.e., solution/glass interface) for membranes S1 and S4.

The formation of the continuous skin for reverse osmosis (RO) membranes has been previously attributed to adsorption processes between the polymer chains in the casting solution and the glass support.[9] In the present case, this is represented in the cross sections of the membranes shown in Figure 2 as the layer at the lower part of each photograph. It can be seen that S1 comprises mainly fine pores, with some large, pear-shaped holes. The pores for the remaining samples S2, S3, and S4 are of similar diameter (about 5 μm). Samples S2 and S3 have a relatively thin bottom layer compared with that for S4, which has the highest DVB/PS ratio. Some pores are occupied in this polymer deposition area [Fig. 2(D)], presumably with partially separated or poorly solvated polymer prior to or at the time of phase inversion. This artifact is not found in other membranes at lower DVB concentrations, nor at higher PS concentrations, so that these particles might also be cross-linked copolymer, rich in DVB.

The cross section of S1 is more clearly shown in

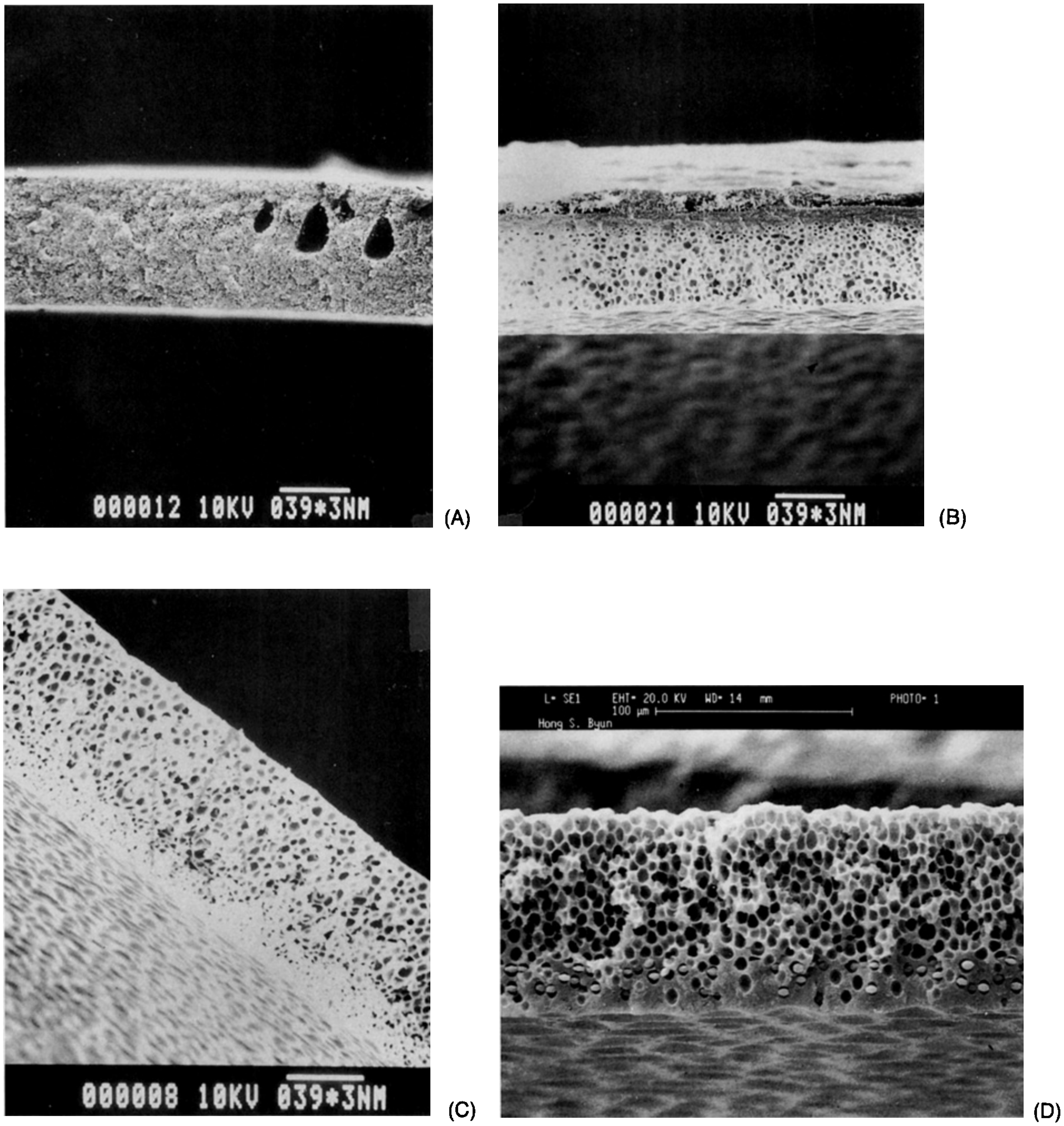

Figure 2 Cross sections of cross-linked asymmetric membranes: (A) S1; (B) S2; (C) S3; (D) S4. Magnification: 600×.

Figure 3. The montage given in Figure 3(A) confirms that skins at both top and bottom are not reasonable at this magnification. Although pore size in the main body of the membrane is not uniform, it appears that the mean diameter decreases at the two surfaces. The interior of a large hole is shown in Figure 3(B) and indicates that the walls of this cavity are also porous.

The top and bottom surfaces of S1 and S4 are shown in Figure 4. Where cross-linker level is low (S1), both surfaces contain holes, with those in the bottom surface being numerous but minute (in the example shown, a pinhole exists at the lower left). There is furrowing, as often found in these surfaces, due to uneven binding to the glass support. The upper surface of S1 contains numerous round holes ranging from 0.5 to 3 μm in diameter. The presence of pores or holes throughout the membrane means that RO performance will be minimal. By analogy with Smolders' findings,[34] local polymer concentra-

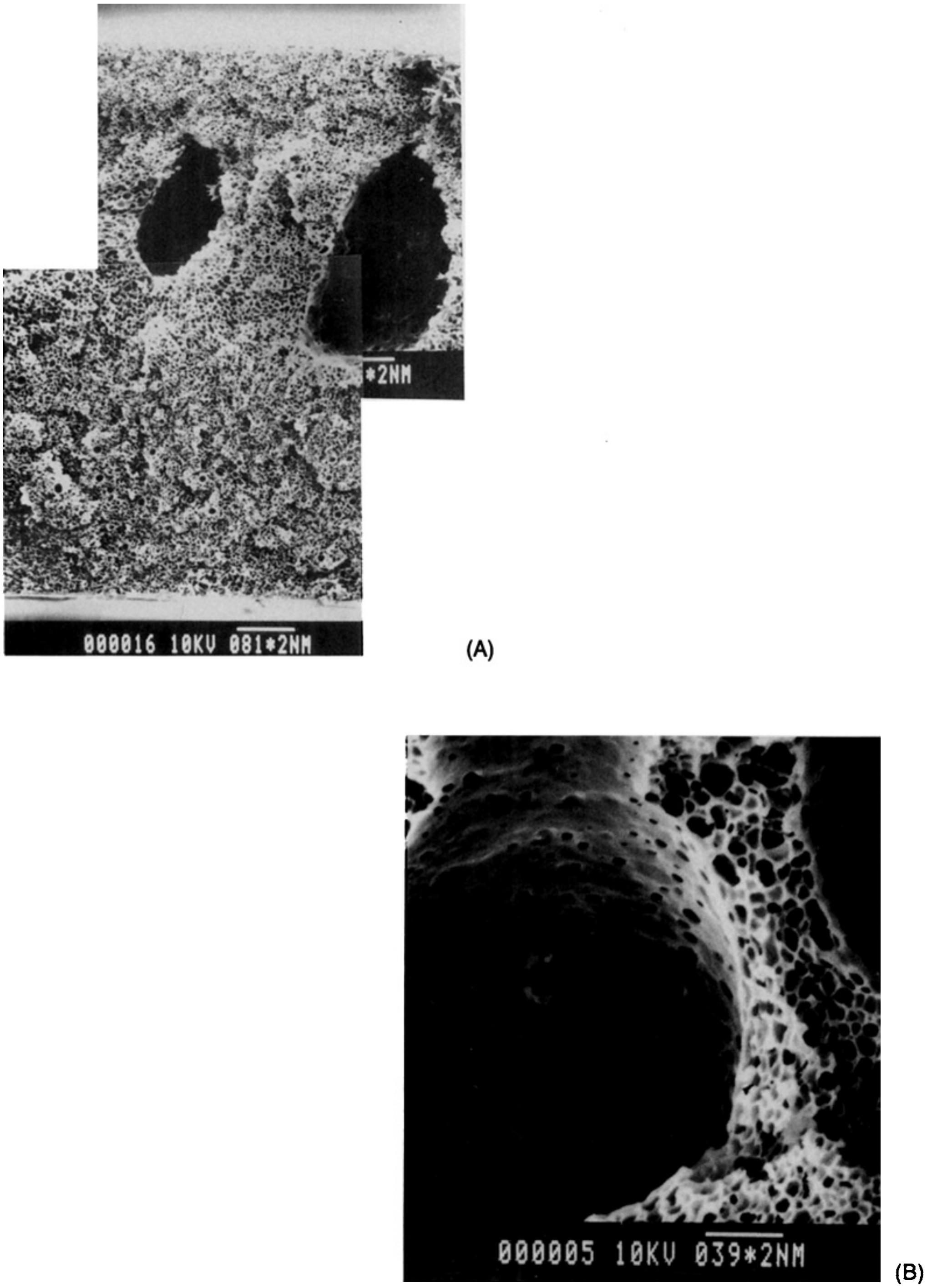

Figure 3 (A) Cross section of S1, 2000×. (B) Enlarged macrovoid, 5800×.

tion at the time of precipitation was insufficient to form a skin, in contrast to the conditions prevailing for membranes S2–S4.

The top surfaces of these membranes were microscopically continuous, except for several macroscopic defects (pinholes). The bottom surfaces were also continuous, although an undulating texture is gradually found. Examples of surfaces are given in Figure 4 for sample S4, although S3, while similar, contained fewer defects. The degree of phase separation and thus membrane morphology not only depends upon dead polymer concentration[9] but also on, according to Okay,[35] cross-linker concentration, concentration and type of diluent, and reaction temperature. This part of our study thus agrees with one facet of Okay's findings.

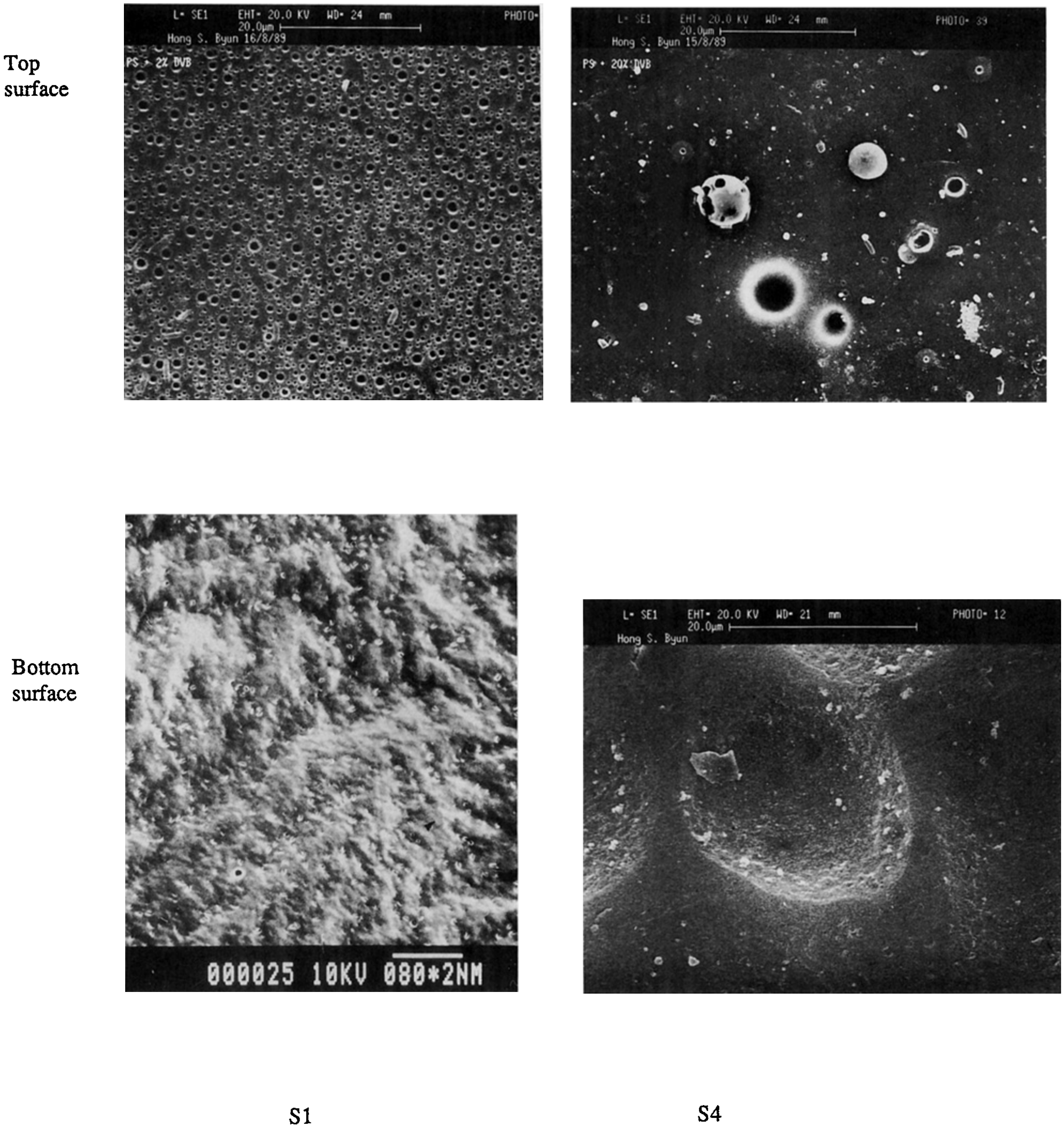

Figure 4 Top and bottom surfaces of S1 and S4 membranes.

Effect of Initial Polystyrene Concentration upon Membrane Morphology

Although this variable has been previously reviewed in some detail,[9] it was thought necessary to examine the effects of very high and low levels of PS, instead of the 25% used in the S1 formulation. Membranes were therefore prepared using 10 and 40 initial wt % PS, and the resulting top and bottom surfaces, with cross sections, are shown in Figure 5. It can be seen that the first membrane has a uniform cross section with moderately large and uniform pores, but both top and bottom surfaces are also highly porous. It should have a high water flux but no selectivity.[36] The 40% initial PS membrane of the S1 type shown at the right of Figure 5 has continuous

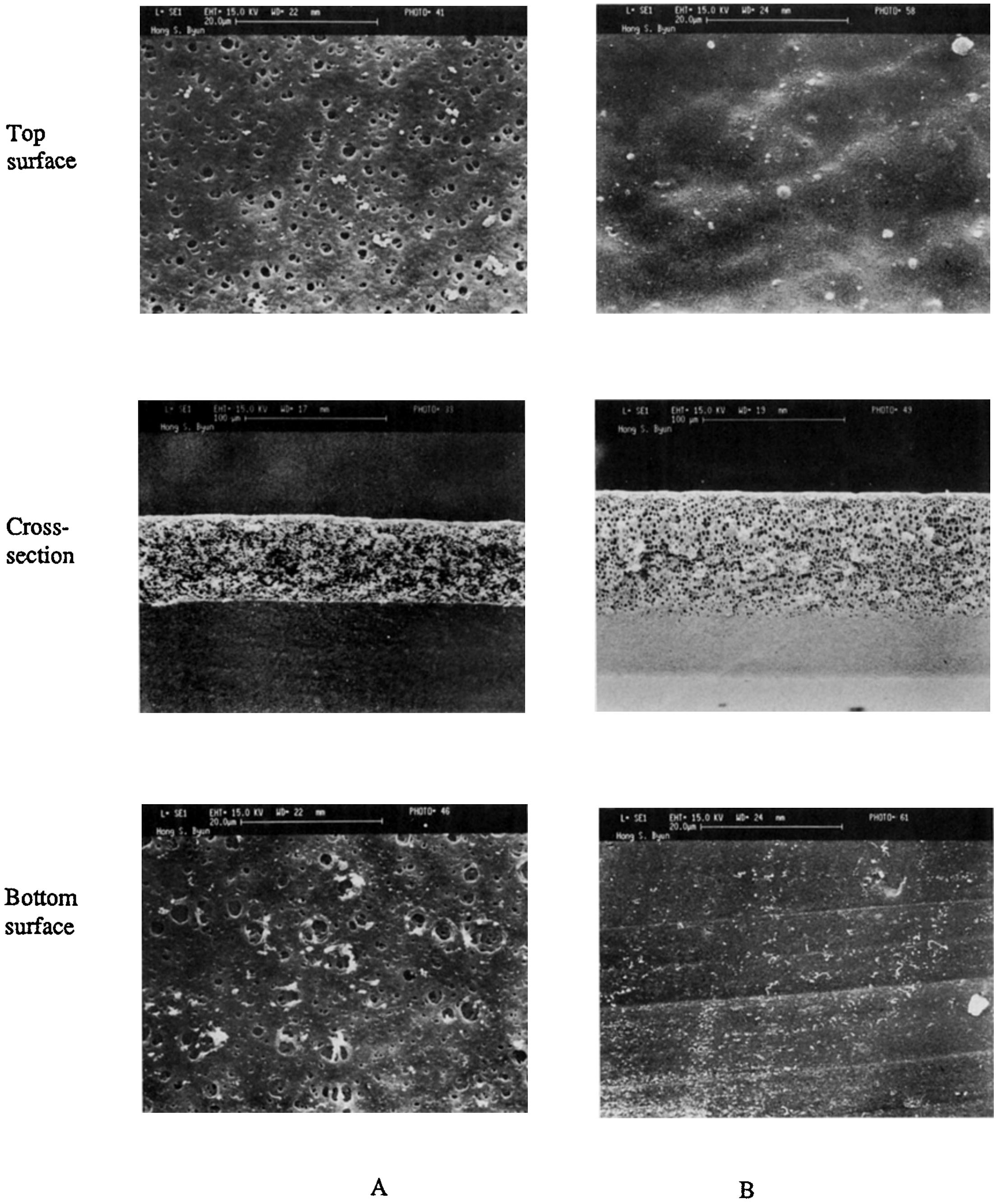

Figure 5 S1-type membranes, with differing initial PS: (A) 10%; (B) 40%.

top and bottom surfaces, but the cross section has a nonporous band composing about one-third (i.e., $\approx 40\ \mu m$) of the total. This lower part can be attributed to the PS being now barely dissolved in the NMP and forms a wide band of viscous sol–gel on the glass. The mass of polymer in this particular formation is much greater than for the 10% PS sample and so the total thickness is correspondingly greater. This membrane will have negligible flux. Thus, both extremes in composition lead to products unsuited for RO, consistent with a previous finding.[9] It is evident that formulations in which 25% initial PS and either 5 or 10% DVB are likely to be the best candidates.

Effect of Low Levels of Elastomer upon Morphology

Although the primary aim was to seek improvements in mechanical behavior, a secondary objective was to determine whether each of these unsaturated additives could be used as a marker. In principle, they can be selectively stained with OsO_4, which would, in cases where strong phase separation occurs, lead to contrast with the rubber-rich regions being

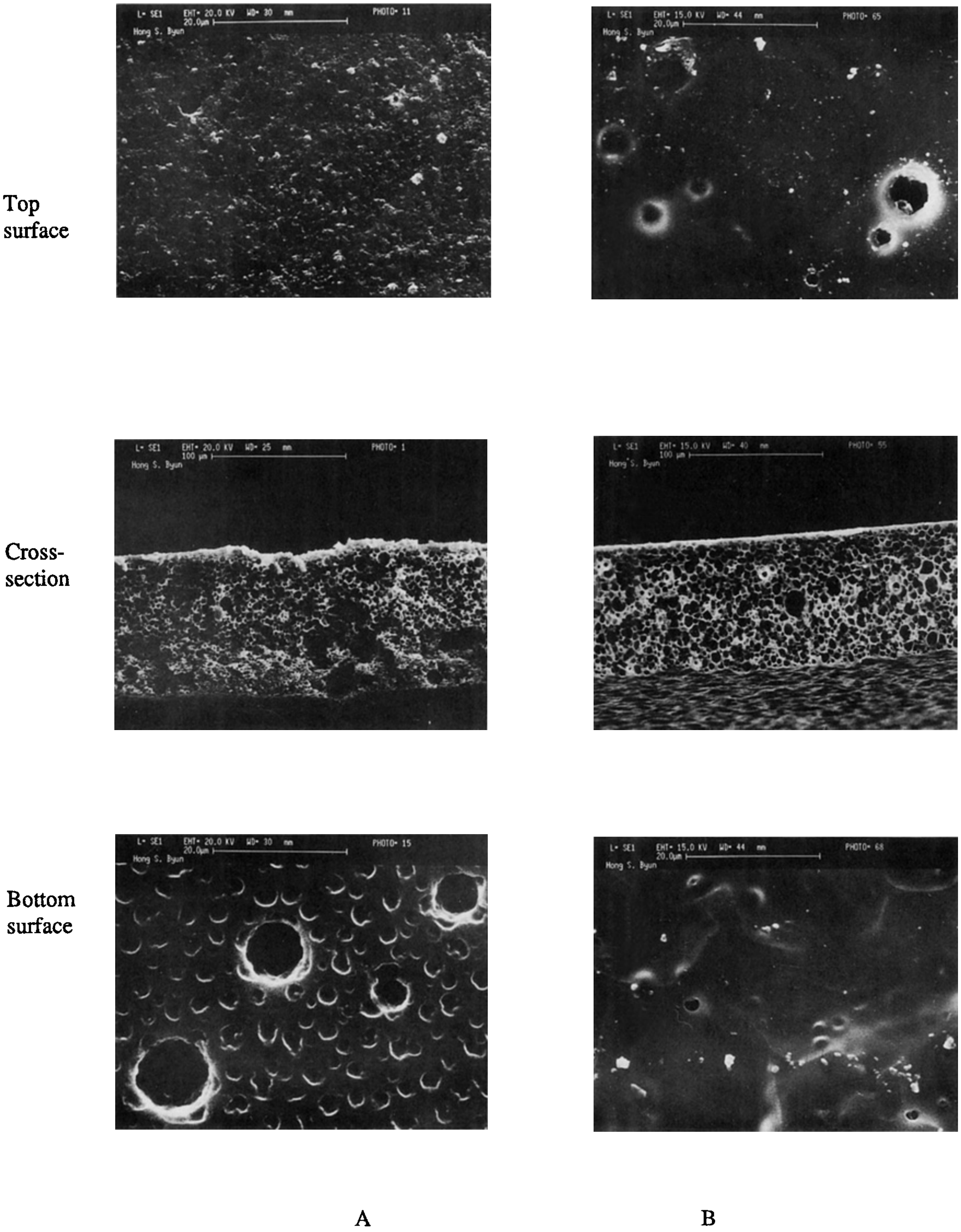

Figure 6 Morphologies of S5 and S6 membranes.

Table II Mechanical Properties of Cross-linked Asymmetric Membranes

DVB Content in Casting Solution (Membrane Code)	Average Tensile Stress at Break, σ_b (MPa)	Average Breaking Strain, ε_e (%)	Average Modulus, E (MPa)
2% (S1)	2.2	1.1	197
5% (S2)	2.9	1.7	244
10% (S3)	3.9	2.4	251
20% (S4)	4.4	2.1	326
SB (S5)	3.3	1.7	278
PBD (S6)	2.5	1.6	234

lighter. In fact, there is some slight "patchiness" in contrast seen in the cross-sectional SEMs in Figure 6, with probable migration of this material to the upper surface. These S5 and S6 membranes are based on the S3 formulation that gave a membrane with satisfactory morphology. The cross sections of S5 and S6 are indeed comparable with S3, although the former have top surfaces containing small (S5) or large (S6) pinholes. However, the pores of S5 and S6 appear uniformly large from surface to surface. This lack of asymmetry is likely to be associated with poor RO performance.

The bottom surface of S6 is convoluted and pinholed and is essentially the same as that of S3. However, that for S5 contains both small and large holes and reflects a quite different polymer/diluent/glass

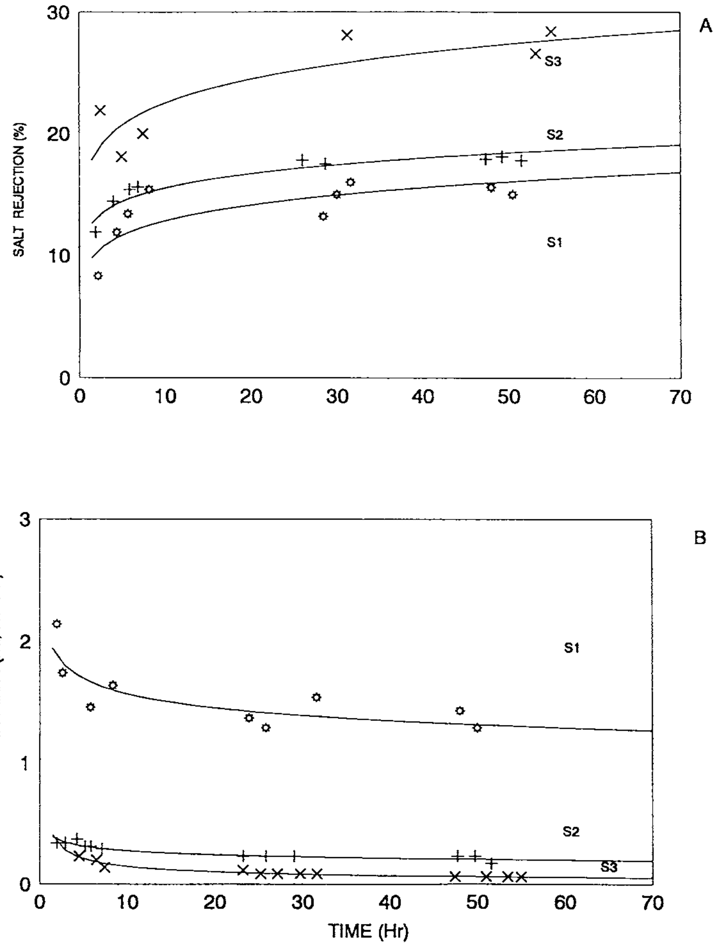

Figure 7 (A) Salt-rejection and (B) water-flux properties of membranes: 0.005 M NaCl; 1.38 MPa.

support history. Further studies on various treated glass and polymeric substrates are underway to better understand the development and control of bottom surface morphologies. In summary, these particular PBD and SB block additions do not possess any advantages. However, further experiments in which higher levels of a wider range of elastomers are justified, as the slight unsaturation that they impart may additionally provide sites for subsequent chemical modification and functionalization.

Mechanical Behavior

Tensile testing of membranes was conducted in a screening capacity, to detect any significant differences in performance. Changes in membrane thickness were incorporated in the δ_b and E calculation. The nominal data given in Table II reveal that the membranes are quite brittle. Increasing DVB increases stiffness and breaking stress, although a maxima in breaking appears to occur below 20% DVB. The low levels of either SB or PBD do not provide properties significantly different from those of S3; indeed, it seems that these membranes are more brittle. At substantial levels of addition (10–20%), one might expect some reduction in strength, but anticipate significant increases in ε_b. As changes in solid polymer density are encountered in the various membranes, as revealed by SEM, detailed analysis of these data is unwarranted.

Reverse Osmosis (RO) Performance

Water flux and salt-rejection properties of membranes are shown in Figure 7 and the effect of degree of cross-linking on RO performance is shown in Figure 8. As DVB concentration increases, salt rejection increases and water flux decreases. For the S1 membrane, initial water flux decline was more evident than with the other membranes (Fig. 7), possibly due to pore compaction at this low degree of cross-linking. However, it should be recognized that the S1 membrane has a much higher water flux, which exaggerates the flux decline problem. On the other hand, a similar amount of foulant on the S2 and S3 membranes would have less impact on the overall "resistance" and therefore less effect on flux. When the membrane contained 20% DVB, there was no measurable water flux at the normal operating pressure of 1.38 MPa or even at 2.76 MPa. This is due to the predominantly closed-cell structure in the bulk and the thick dense structure at the bottom side.

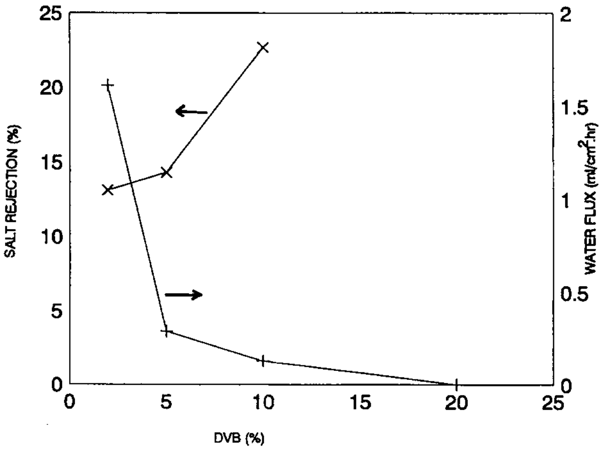

Figure 8 Effect of cross-linker concentration on RO performance, 0.005M NaCl at 1.38 MPa.

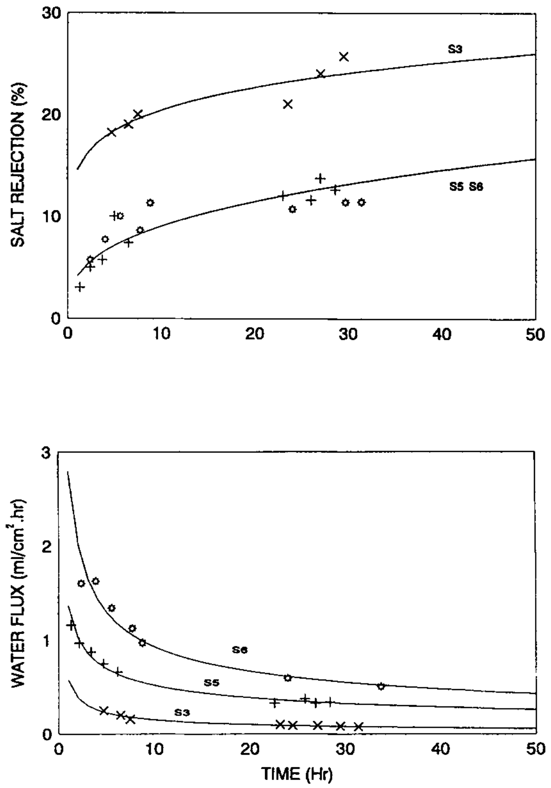

Figure 9 RO performance: 0.005M NaCl at 1.38 MPa.

The variation of RO performance with different casting compositions is shown in Figure 9 and correlates well with electron microscope results. The lower water flux of the S5 membrane may be due to a slight densification at the bottom surface. However, all tested membranes have shown very low salt rejection, due to either pinholes or pores in the top surface not resolved in the electron microscope. For example, a pore of 5 nm is not easily observed using electron microscopy but allows high permeation of

NaCl. Although the performance characteristics for these nontreated membranes is quite poor, they are potentially suitable substrates for subsequent modification, to give enhanced performance. The performance of sulfonated membranes is, in fact, markedly improved, with details published separately.[37]

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