

# Sulfonation of Cross-Linked Asymmetric Membranes Based on Polystyrene and Divinylbenzene

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## SYNOPSIS

Asymmetric microporous membranes based on polystyrene cross-linked with divinyl benzene were prepared. They were sulfonated with sulfonic acid and washed with solutions of gradually increasing pH to reduce environmental shock. The sulfonation was monitored by infrared spectroscopy, and changes in wettability and sulfur content were also recorded. Morphologies and reverse osmosis performance of sulfonated membranes were measured, with both water flux and salt rejection increasing after treatment.

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## INTRODUCTION

In a previous article,<sup>1</sup> the preparation of cross-linked/asymmetric membranes based on polystyrene and divinylbenzene using UV radiation was described. Their performance as reverse osmosis (RO) membranes was inadequate, indicating that modification was needed to raise the performance to satisfactory levels.

Recently, emphasis has shifted from new membrane development to membrane modification,<sup>2-5</sup> with common methods being cross-linking, radiation grafting, surface oxidation, plasma-phase reaction, and surfactant adsorption followed by copolymerization. Among these modification techniques, the last is most widely used because of the excellent workability and low cost of operation, but it has the limitation that the treated surface may not be durable. The process of surface oxidation (i.e., by a wet process) is less useful due to its poor workability.

Chemical cross-linking considerably improves the

selective permeability of poly(vinyl alcohol) (PVA) to water and salts. Thus, PVA membranes cross-linked with formaldehyde were shown<sup>6</sup> to have salt rejections of 93–97% and water-absorption permeabilities of  $4-8 \times 10^{-8}$  cm<sup>2</sup>/s (approximately equal to 0.11–0.22 l/m<sup>2</sup> h). Even better results were obtained by Dick and Nicolas<sup>7</sup> with tolylene diisocyanate cross-linked PVA membranes, where salt rejections of up to 99.2% and water permeability coefficients in the range of  $2-5 \times 10^{-7}$  cm<sup>2</sup>/s (approximately equal to 0.55–1.39 l/m<sup>2</sup> h) were reported. Cross-linking with polyvalent metal ions enhances the chemical resistance and mechanical strength of PVA membranes,<sup>8</sup> so that H<sub>3</sub>BO<sub>3</sub>-complexed products have a flux of 6.3–10.4 l/m<sup>2</sup> h and retention of 90–95% at pH 12. Very little pore compaction occurred, reflecting improved mechanical strength due to cross-linking.

Although graft copolymers combine the properties of their polymeric constituents and so potentially offer a wide spectrum of properties, they are only used commercially in limited applications. Most membranes are made at very high graft yields<sup>9-12</sup> and, consequently, the bulk properties of the base polymer are altered. It was reported<sup>13</sup> that flame

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and acid resistance increased when aromatic polyamide was UV-grafted with tetrafluoroethylene, but the aromatic polyamide fabric darkened. When the silicone rubber tube was  $\gamma$ -grafted with *N*-vinylpyrrolidone, the thromboresistance of the silicone rubber was improved,<sup>14</sup> but the silicone tube became brittle at higher degrees of grafting. Limitations can be avoided if grafting is continued to the surface.

Plasma deposition of polymers onto appropriate microporous substrate membranes has been extensively investigated<sup>15,16</sup> because of their unique properties, being very different from conventionally prepared polymers. These methods lead to high degrees of branching and cross-linking, high concentrations of residual free radicals, and high degrees of monomer fragmentation. However, plasma-modified RO membranes are relatively new and at an early stage of development.

Sulfonation is a powerful and versatile polymer modification tool, since it not only greatly increases the affinity for water, but can also be applied to a wide range of polymers. Sulfonated polymers can be prepared as free acid ( $-\text{SO}_3\text{H}$ ), salt ( $-\text{SO}_3\text{Na}^+$ ), or ester ( $-\text{SO}_3\text{R}$ ),<sup>17</sup> at high or low degrees. Polymers can be sulfonated before fabrication, or the fabricated article can be sulfonated either uniformly or on the surface only.

Ion-exchange membranes consist of cross-linked polymer networks with ionized or ionizable groups. The functional groups can ionize into a fixed ion, attached to the polymer chain and a counter- or co-ion, which is mobile and can diffuse through the swollen membrane and exchange with an ion of like charge in a surrounding solution. Separation properties of these membranes are determined by the charge and concentration of ions in the surrounding solution and in the membrane structure. Most of the early ion-exchange membranes were produced from phenolsulfonic acid cross-linked with formaldehyde but were very brittle and not used.<sup>18</sup> Stronger

cation-exchange membranes are made with sulfonated polystyrene (PS), whereas anion-exchange membranes are prepared from chloromethylated PS followed by amination with a tertiary amine.<sup>19</sup>

Conventional sulfonation may be carried out with sulfuric acid, sulfur trioxide, oleum, or chlorosulfonic acid or with mixtures.<sup>20,21</sup> Although sulfonation of styrene-divinylbenzene (DVB) membranes is a commercial example of introduced ionic functionality to preformed cross-linked polymers, obtaining intimate molecular contact between aromatic sites in the cross-linked polymer and the sulfonating agent molecules may be a problem. Generally, surface layers of the copolymer swell in sulfuric acid upon sulfonation, exposing the next layer to the reagent. As a result, sulfonation finally occurs relatively uniformly throughout the copolymer membrane. Chlorosulfonic acid/carbon tetrachloride mixtures encourage reaction product swelling, resulting in the highest degree of sulfonation.<sup>22</sup> Organic swelling agents in the synthesis of sulfonated resins improve the physical properties of the finished product and increase reaction rates, thus reducing the formation of extra sulfur cross-links.<sup>23,24</sup>

In our work, cross-linked asymmetric membranes cast from the solutions containing 5 and 10% DVB<sup>1</sup> were selected for modification, because they already had adequate water flux and salt rejection and showed little initial water-flux decline.

## EXPERIMENTAL

### Membranes

Cross-linked asymmetric membranes were prepared from a mixture of PS, styrene monomer, DVB cross-linker, benzoin photoinitiator, and *N*-methyl-2-pyrrolidone (NMP) diluent. The compositions of mixture are as follows:

Membrane Code	PS	DVB	Styrene	NMP	Benzoin
S2	25%	5%	44.2%	25.3%	0.5%
S3	25%	10%	41.0%	23.5%	0.5%

These solutions were stirred for 24 h in darkness and then spread with a glass rod onto a glass plate framed with a 75 mm-thick PTFE sheet to give a 5 × 5 cm liquid film. The cast solution was then ex-

posed to UV light to form partially cross-linked sol. The partially polymerized films were then coagulated in methanol containing benzoin. An additional 24 h exposure to UV light was used to form the final

structure. Further preparation details are described elsewhere.<sup>1</sup>

### Sulfonation

Conditions were selected in which sulfone bridge formation is minimized. Thus, sulfonation was carried out at 30°C using concentrated sulfuric acid (98.1%) and continuous stirring. A large excess of sulfuric acid (~ 700 mL of sulfuric acid/~ 0.1 g of dry membrane) was used to remove the water formed in the sulfonation step. Various reaction times with sulfuric acid (4, 8, and 24 h) were employed and the extent of modification for each treatment was assessed by various methods as listed below.

After each reaction time had elapsed, the treated membranes were washed by slow dilution with water (i.e., 75, 50, 25, and 5% aqueous sulfuric acid) to minimize cracking caused by differential swelling ("osmotic shock"). Precautions were taken to minimize sudden changes in the environment, although these cross-linked membranes are likely to be more resistant to osmotic shock than are conventional polymers. Sulfonated membranes were then washed in distilled water and 20% aqueous NaOH.

Several experiments were carried out to verify the degree of sulfonation. Treated membrane, 1 × 1 cm squares, were weighed after vacuum drying at 25°C for at least 1 week, immersed in water at 25°C, and reweighed after equilibration and removal of superficial water. The swelling ratio, *S*, is given as a percentage of water relative to dry membrane weight. The ion-exchange capacity was measured by immersing about 1 mg of the acid form of the membrane in a 20 mL solution of 0.005*N* NaOH overnight, with continuous stirring. A 10 mL aliquot was backtitrated with 0.005*N* HCl to a pH of 7.0. Blank tests and an average of five results was used to reduce the experimental errors during the backtitration. Ion-exchange capacity were reported as milliequivalent per gram of dry membrane.

The water contact angle was measured using the sessile drop method<sup>25</sup> as it is quick and simple. A water drop was placed onto a membrane and an angle reading taken within 10 s. All results presented are an average of at least five measured angles with water drops placed on three different regions on the membrane.

Infrared absorption spectra were recorded from 400 to 4000 cm<sup>-1</sup> by means of a grating IR spectrophotometer (Perkin-Elmer Model 457). The dried sulfonated membranes were powdered with a mortar and pestle at liquid nitrogen temperature. Three milligram samples were then intimately mixed with

200 mg dry KBr, and the mixture was subjected for 5 min to a pressure of approximately 10 tons in an evacuated die, producing 13 mm-diameter transparent discs.

The relative amounts of sulfur in treated membranes were measured using an energy dispersive X-ray analyzer (Jeol JXA-840 LINK SYSTEM AN 10000). A carbon coater (SPEEDIVAC, Edwards High Vacuum Ltd.) was used to render samples conductive prior to analysis.

The morphology of dried membranes was determined by SEM after fracturing in liquid nitrogen. Jeol JXA-840 and Cambridge 360 microscopes were used. Samples were coated with gold-palladium using a "Polaron" sputter coater. RO performance of sulfonated cross-linked membranes were determined using a small static RO cell described by Kopecek and Sourirajan.<sup>26</sup>

## RESULTS AND DISCUSSION

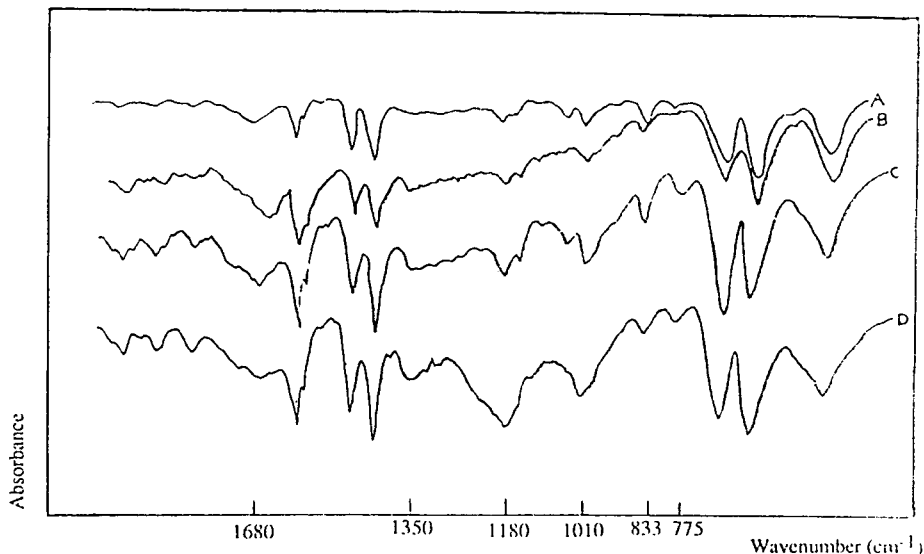
### Infrared Spectra

Changes in amounts of monosubstituted vinyl groups associated with the cross-linker and reflected by absorbances at 1680 cm<sup>-1</sup> and changes in sulfonation, reflected by peaks at 1180 and 1010 cm<sup>-1</sup>, can be seen in the IR spectra included in Figures 1–3.

In the first case, the increasing intensity of the 1680 cm<sup>-1</sup> peak with increased added DVB indicates that much of this has been incorporated as vinyl side groups or grafts rather than as cross-links (where only disubstituted double bonds will occur). These unreacted pendent vinyl groups (Fig. 4) have been reported by Bertholin et al.<sup>27</sup> and Wiczorek et al.<sup>28</sup> and greatly affect the properties and structure of the membrane during the sulfonation of the cross-linked membrane.

After sulfonation, the IR spectra [Figs. 1 (C) and (D), 2(B)–(D), and 3(C) and (D)] possess new peaks at 1180 and 1010 cm<sup>-1</sup> due to the symmetric and asymmetric vibration of sulfonate groups.<sup>29</sup> An additional peak at 1350 cm<sup>-1</sup> also appears, this being the antisymmetric vibration of diarylsulfone,<sup>30</sup> the "sulfone bridge."

A strong peak at 833 cm<sup>-1</sup> compared to a small peak at 775 cm<sup>-1</sup> indicates that the substitution on the benzene ring is mainly in the *para* position. In summary, the sulfonated cross-linked membranes contain aromatic rings substituted with —SO<sub>3</sub>H groups, unsubstituted rings, and a small number of sulfone bridges.

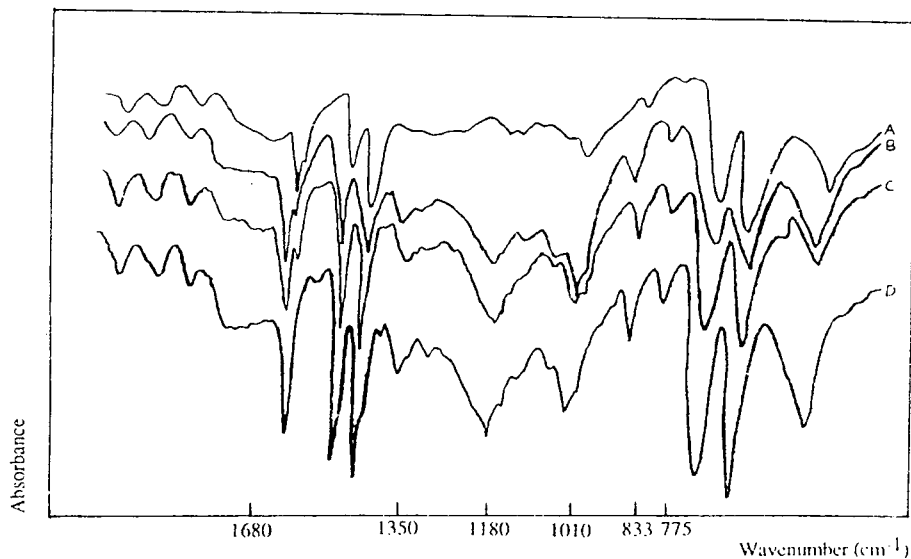


**Figure 1** IR spectra of (A) S1 membrane, (B) sulfonated S1 membrane for 4 h (S1-1H), (C) sulfonated S1 membrane for 8 h (S1-2H), and (D) sulfonated S1 membrane for 24 h (S1-3H).

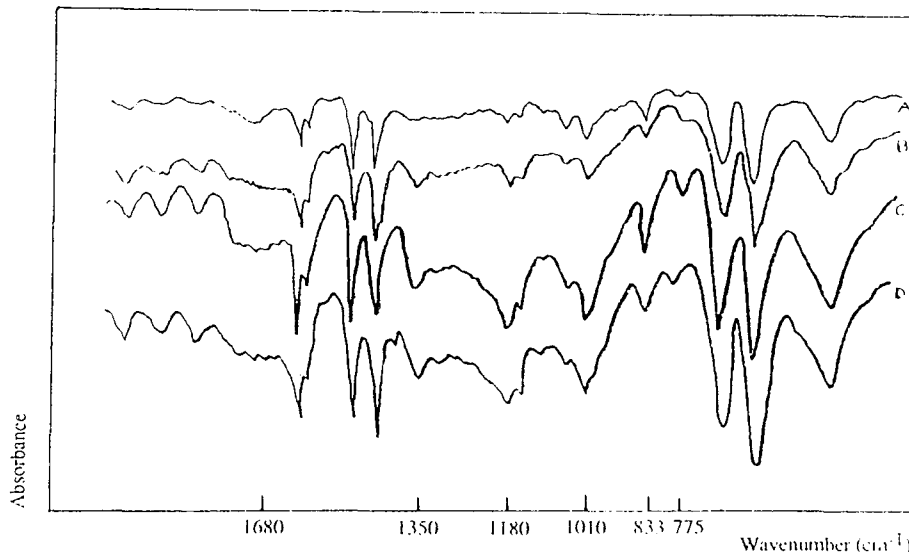
### Ion-exchange Capacity, Swelling, and Contact Angle Measurements

The effects of cross-linking degree and reaction time with sulfuric acid on the ion-exchange capacity are summarized in Figure 5 and Table I and show that the higher cross-linked membrane has the more sulfonated groups.

The swelling ratio data shown in Figure 6 indicate that untreated cross-linked membranes show a decreased swelling ratio with increased cross-linking. This is attributed to an increase in tightness of the network. These trends are in agreement with previous work<sup>31-33</sup> and also attributed to changes in chain stiffness. Levels of swelling in the highly cross-linked regions under these conditions are low.<sup>34</sup>



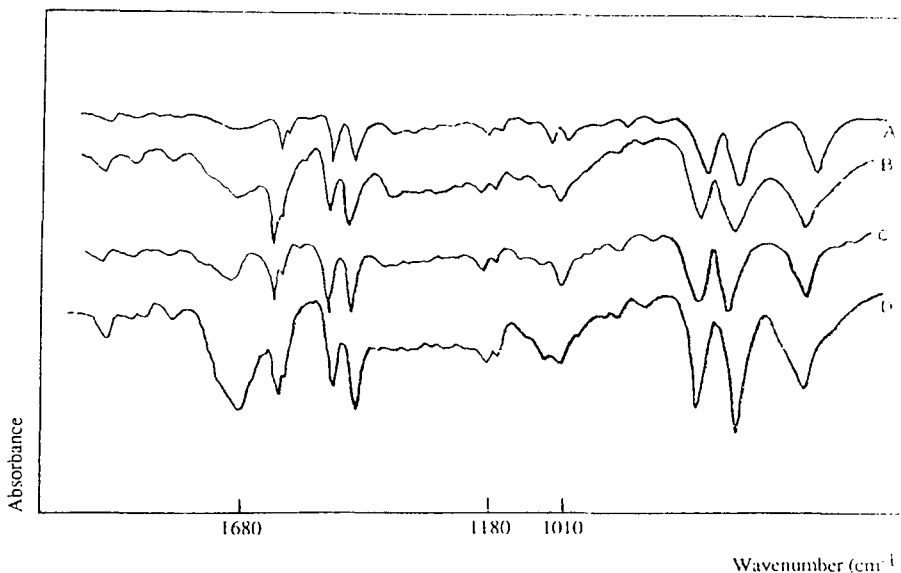
**Figure 2** IR spectra of (A) S2 membrane, (B) sulfonated S2 membrane for 4 h (S2-1H), (C) sulfonated S2 membrane for 8 h (S2-2H), and (D) sulfonated S2 membrane for 24 h (S2-3H).



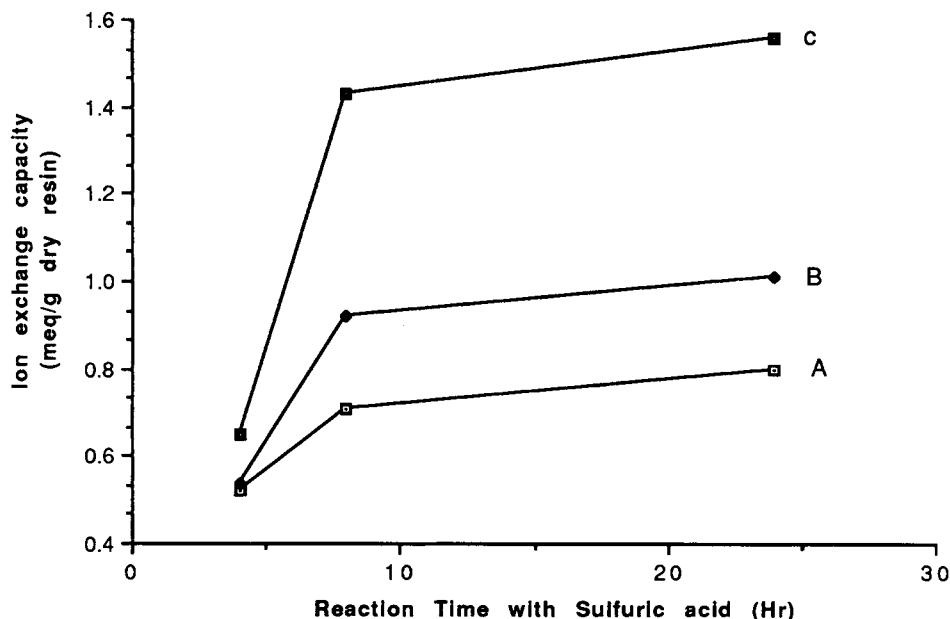
**Figure 3** IR spectra of (A) S3 membrane, (B) sulfonated S3 membrane for 4 h (S3-1H), (C) sulfonated S3 membrane for 8 h (S3-2H), and (D) sulfonated S3 membrane for 24 h (S3-3H).

However, after sulfonation, the opposite trend was found. The significant increases in swelling ratio with DVB may reflect an increased reaction between the bridging molecules and the sulfuric acid, counteracting any reduced access to reagent within the more constricted network. There are also two other structural possibilities, these being pendant groups formed by uncross-linked DVB (i.e., acting as mon-

ofunctional grafts) and also the formation of intramolecular cyclization products, as described in Odian.<sup>35</sup> Whereas Pepper<sup>21</sup> indicates that sulfonation decreases with increased DVB cross-linking, others<sup>36,37</sup> show, also using beads, that the cation-exchange capacity of PS-co-DVB after sulfonation increases with increased cross-linking, in agreement with our own data.



**Figure 4** IR spectra of (A) S1 membrane, (B) S2 membrane, (C) S3 membrane, and (D) S4 membrane.



**Figure 5** Cation-exchange capacity of sulfonated cross-linked membranes containing (A) 2% DVB (S1), (B) 5% DVB (S2), and (C) 10% DVB (S3) with increasing exposure time to sulfuric acid.

With higher levels of ionic sulfonate groups, hydrophilicity increases, as reflected by the water-uptake data. The trend found for the swelling ration were mirrored by the contact angle data (Fig. 7), with the contact angle decreasing with increased cross-linking and sulfuric acid reaction time. This further confirms that sulfonation increases with increased DVB content.

#### Reverse Osmosis (RO) Performance

Performance of treated and untreated S2 and S3 membranes with sulfuric acid are shown in Figures

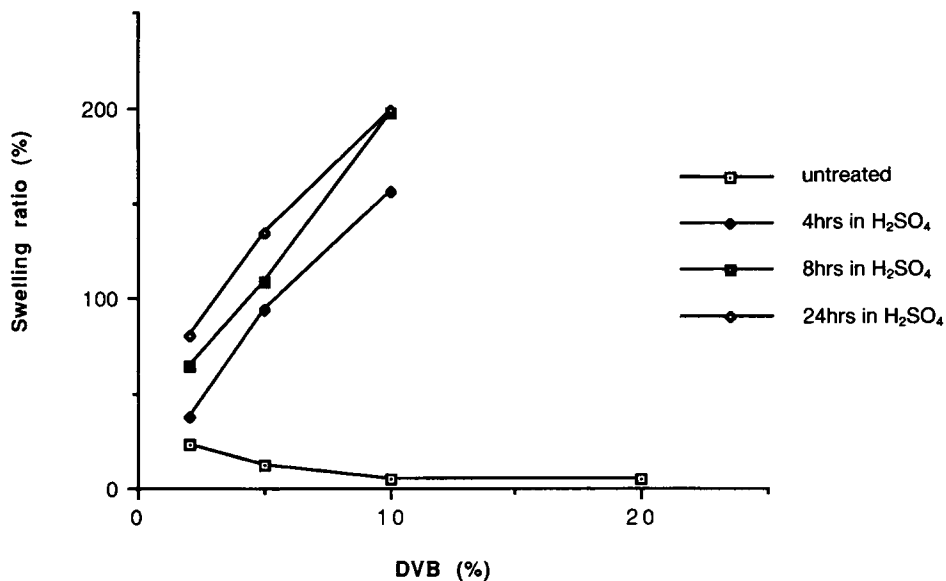
8 and 9, respectively. Sulfuric acid treatment enhanced performance as reflected both in higher water flux and salt rejection. It will be remembered that the original substrate membranes showed the best (but low) properties as previously described.<sup>1</sup> The enhancement in performance is quite dramatic and has transformed the previously unpractical membranes into legitimate reverse osmosis candidates.

#### Membrane Microstructure

The morphology of a typical sulfonated cross-linked membrane is shown in Figure 10(A)–(C). The top

**Table I** The Effects of Cross-linking Degree and the Reaction Time with Sulfuric Acid on the Cation-exchange Capacity

Membrane Code	DVB (%)	Reaction Time with Sulfuric Acid	Cation-exchange Capacity (meq/g Dry Resin)
S1-1H membrane	2	4	0.52
S2-1H membrane	5	4	0.54
S3-1H membrane	10	4	0.65
S1-2H membrane	2	8	0.71
S2-2H membrane	5	8	0.92
S3-2H membrane	10	8	1.01
S1-3H membrane	2	24	0.8
S2-3H membrane	5	24	1.01
S3-3H membrane	10	24	1.56

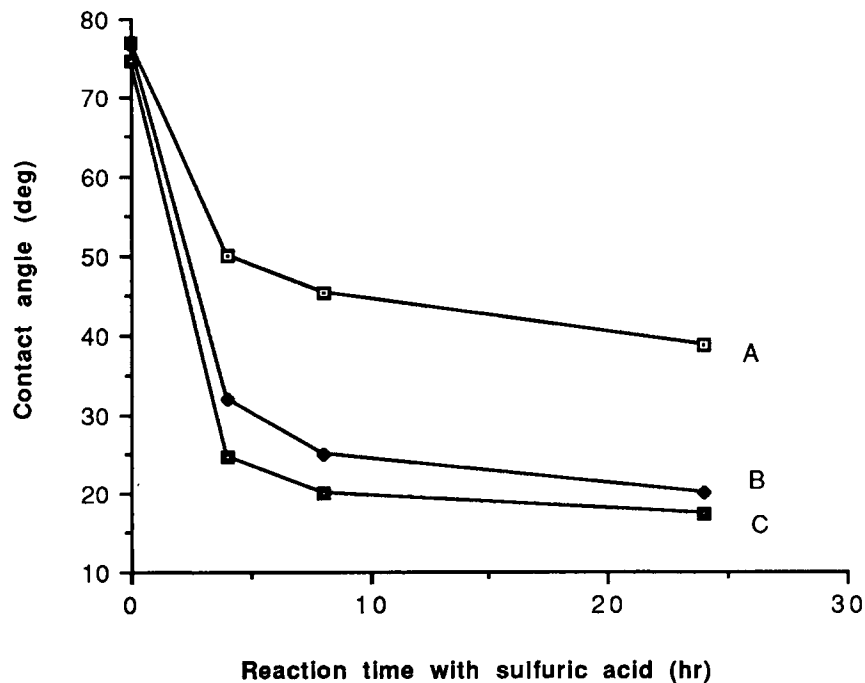


**Figure 6** The effects of cross-linking degree and sulfonation on the swelling ratio.

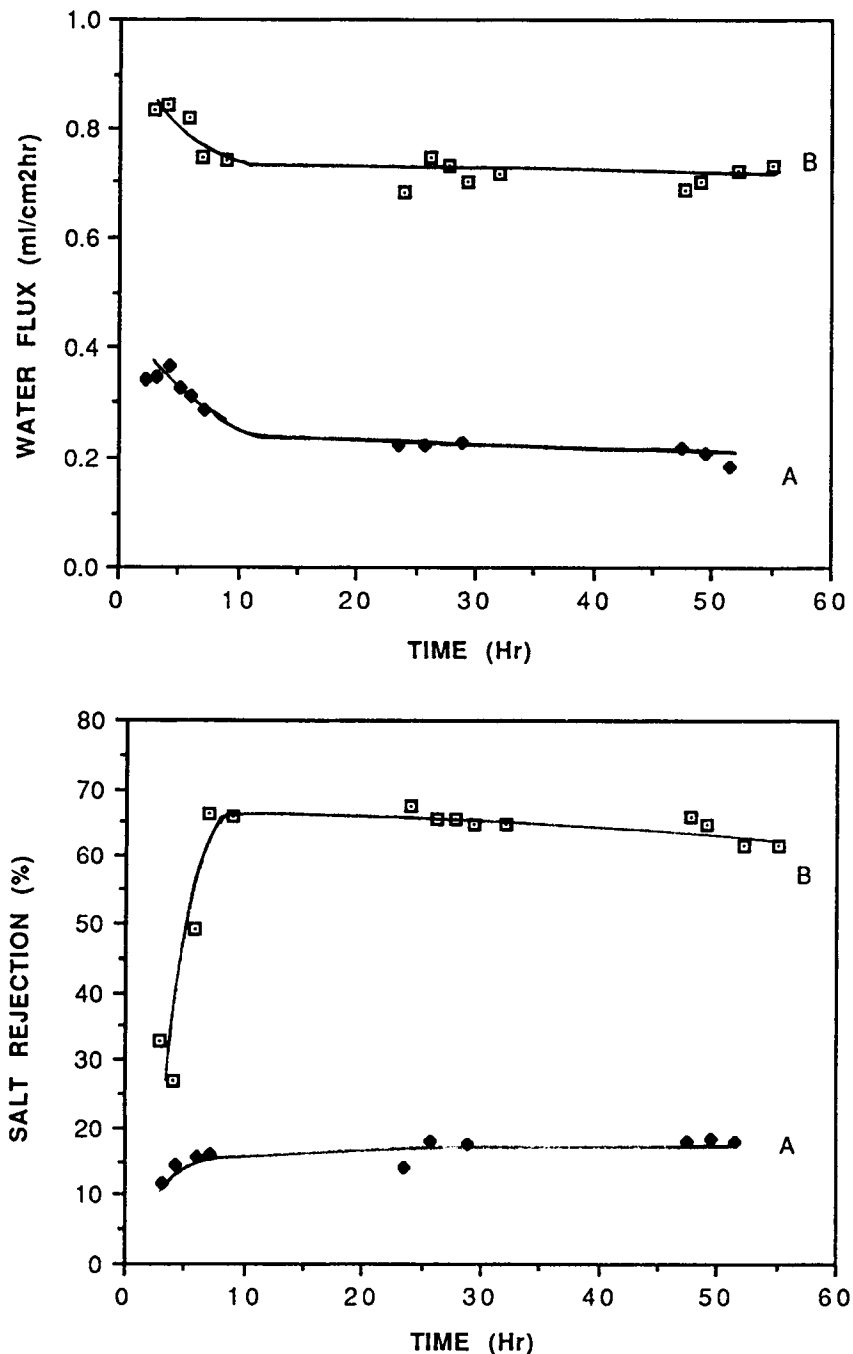
surface is now characterized by numerous pores up to several microns in diameter and this is much more vesicular than is the untreated membrane [Fig. 3(C) in Ref. 1]. This surface alteration may be due to some etching or leaching during the treatment pro-

cess. Energy dispersive X-ray spectroscopy (EDS) reveals that the highest levels of sulfur occur at the top surface, with reducing levels at the bottom.

However, the cross-section and bottom layer [Fig. 10(A) and (B)] are essentially unaltered morpho-



**Figure 7** Changes in contact angle of the membranes containing (A) 2% DVB (S1), (B) 5% DVB (S2), and (C) 10% DVB (S3) with sulfonation hours.



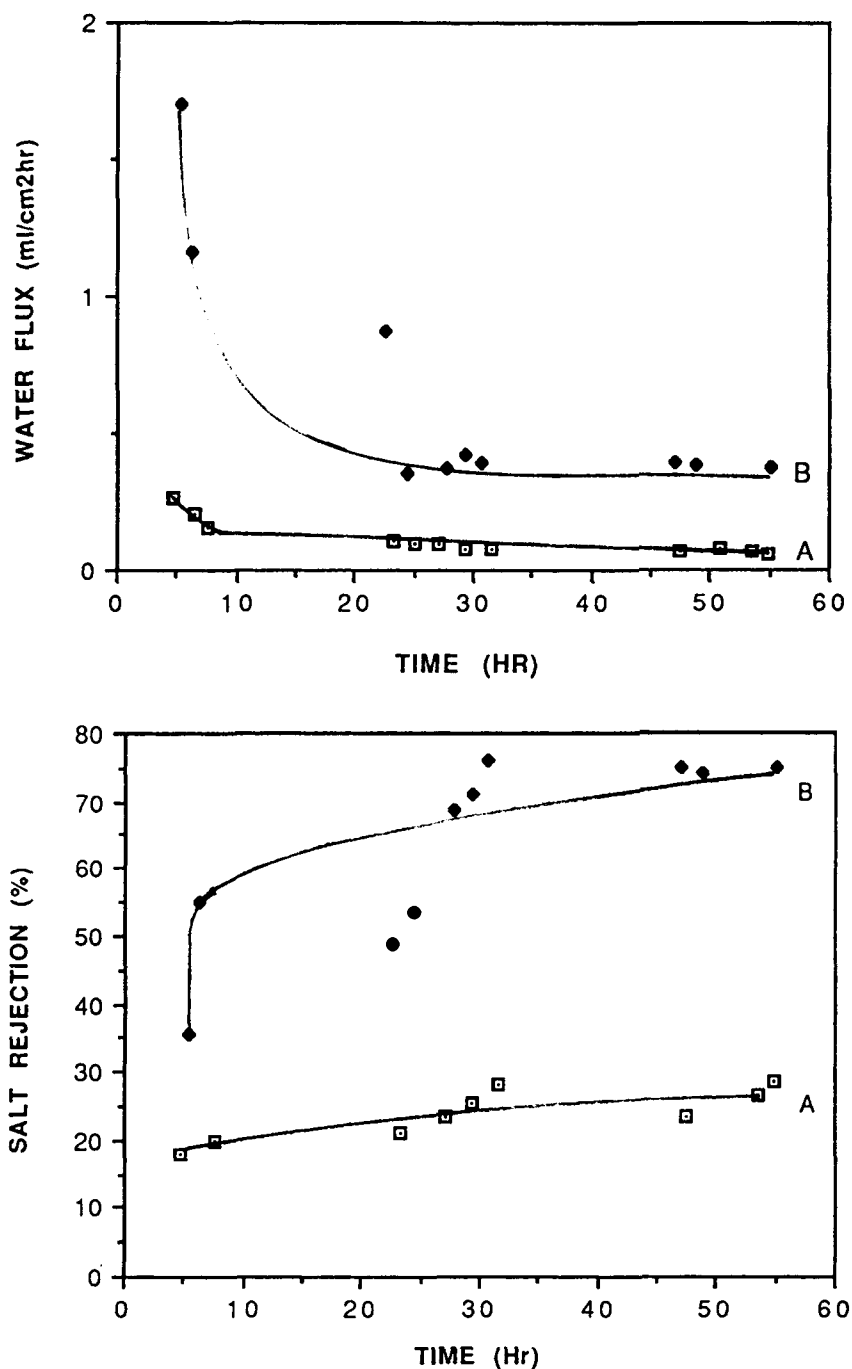
**Figure 8** Water flux and salt rejection of (A) S2 membrane and (B) sulfonated S2 membrane for 8 h (S2-2H membrane) with 0.005M NaCl at room temperature and 1.38 MPa.

logically, and no evidence of internal pore structure disruption can be found. Thus, whereas the altered water flux might be attributed in part to top surface morphology, the dramatic changes found, particularly, in salt rejection, are primarily due to the sulfonation itself.

#### Energy Dispersive X-ray Spectroscopy (EDS)

Whereas some structural information concerning sulfonation has previously been given using IR spectroscopy, EDS is useful in giving semiquantitative estimates of absolute sulfur contents that can





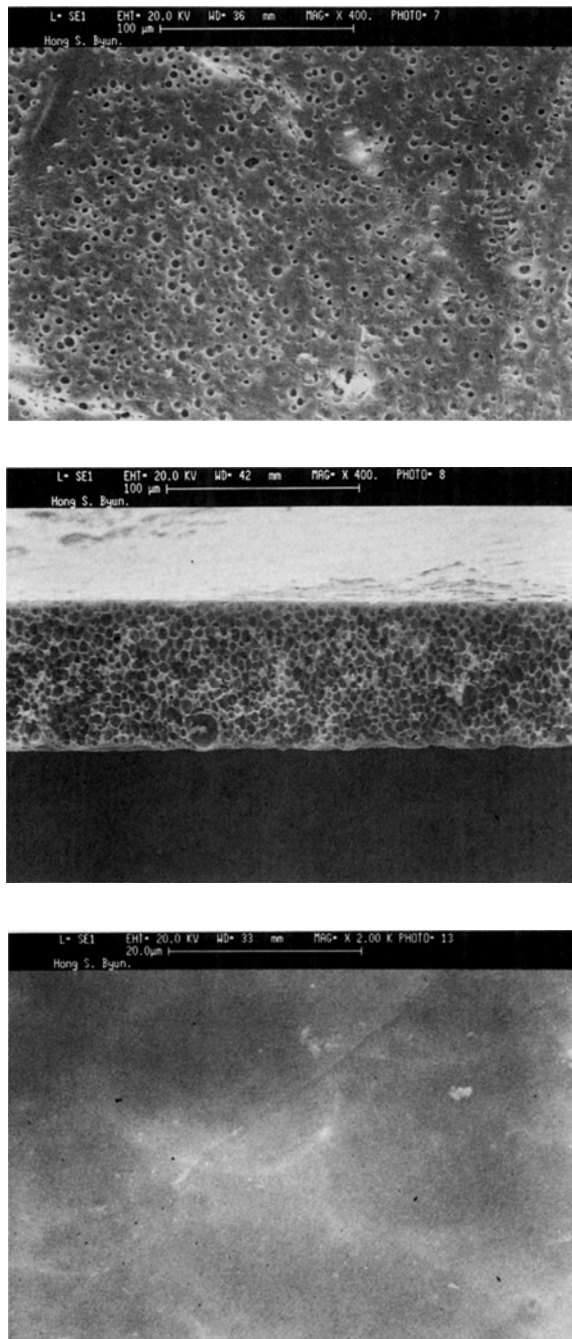
**Figure 9** Water flux and salt rejection of (A) S3 membrane and (B) sulfonated S3 membrane for 8 h (S3-2H membrane) with 0.005 M NaCl at room temperature and 1.38 MPa.

be related to levels of sulfonation. The top surfaces of each of the four levels of DVB cross-linked membranes (i.e., S1–S4) after 8 h treatment with sulfuric acid were analyzed and the spectra are shown in Figure 11. It can be seen that the background counts are comparable for each sample, but that the sulfur

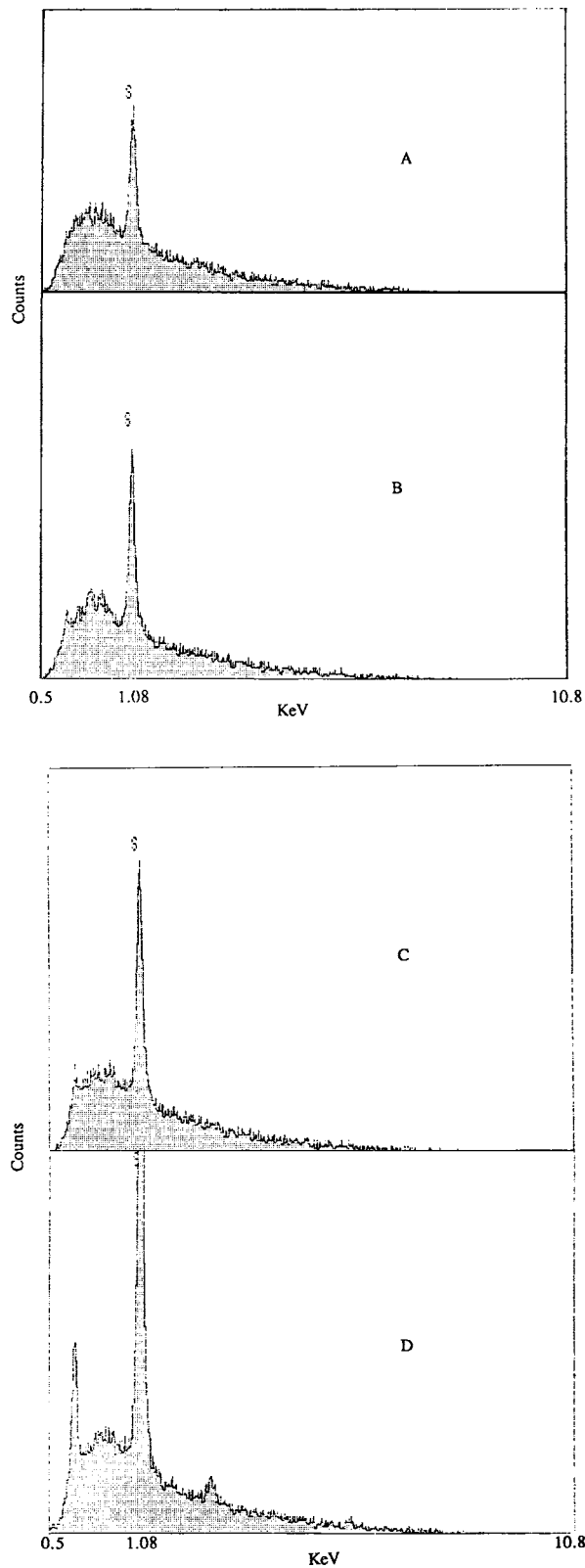
$K_{\alpha}$  peak at 2.30 keV increases with increased DVB level.

In summary, from this work, we believe that the uncross-linked DVB pendant groups have a significant role, and some IR evidence for these has been previously shown (Fig. 4). Clearly, further work is

needed to provide an unambiguous picture of the detailed molecular structure of these systems. For example, solid-state NMR, FTIR, and other techniques would prove useful but are beyond the scope



**Figure 10** Electron micrographs of the S3-2H membrane: (A) top surface; (B) cross-section, top side uppermost; (C) bottom surface. The scale bars correspond to 100  $\mu\text{m}$  for (A) and (B) and 20  $\mu\text{m}$  for (C). Magnifications are 400 $\times$  for (A) and (B) and 2000 $\times$  for (C).



**Figure 11** Energy Dispersive X-ray Spectroscopy of the top surface of (A) S1-2H membrane, (B) S2-2H membrane, (C) S3-2H membrane and (D) S4-2H membrane.

of this work. The performance data and analysis so far performed give a strong indication of increased sulfonation and associated membrane properties at different levels of DVB.

## REFERENCES

1. H. S. Byun and R. P. Burford, *52*, 813 (1994).
2. R. W. Baird, *Radiat. Phys. Chem.*, **19**, 113 (1982).
3. A. Bozzi and A. Chapiro, *Eur. Polym. J.*, **23**, 255 (1987).
4. I. Masahiro and I. Ryuzo, *Makromol. Chem. Rapid Commun.*, **8**, 569 (1987).
5. T. Hirotsu, *J. Appl. Polym. Sci.*, **34**, 1159 (1987).
6. C. T. Chen, Y. T. Chang, M. C. Chen, and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **17**, 789 (1973).
7. R. Dick and L. Nicolas, *Desalination*, **17**, 239 (1975).
8. S. Peter, N. Hese, and R. Stefan, *Desalination*, **19**, 161 (1976).
9. A. Shindler, M. Gratzl, and K. L. Platt, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 1541 (1977).
10. C. H. Ang, N. P. Davis, J. L. Garnett, and N. T. Yen, *Radiat. Phys. Chem.*, **9**, 831 (1977).
11. N. P. Davis, J. L. Garnett, and R. G. Urganhart, *J. Polym. Sci. Polym. Symp.*, **55**, 287 (1976).
12. K. Hayakawa, K. Kawase, and H. Yamakita, *J. Polym. Sci. Part A-1*, **8**, 1227 (1970).
13. M. S. Toy, R. S. Stringham, and F. Dawn, *J. Appl. Polym. Sci.*, **21**, 2583 (1977).
14. A. Chapiro, *Eur. Polym. J.*, **19**, 859 (1983).
15. Y. Osada, Y. Iriyama, and M. Ohta, *Nippon Kagaku Kaishi*, 831 (1983).
16. H. Yasuda, *Radiat. Phys. Chem.*, **9**, 805 (1977).
17. A. F. Turbak and A. Novhay, U.S. Pat. 3,206,492 (Sept. 14, 1965).
18. H. Z. Friedlander, Ed., *Encyclopedia of Polymer Science and Technology*, Wiley, New York, 1968, Vol. 8, p. 620.
19. F. Helfferich, Ed., *Ion Exchange*, McGraw-Hill, New York, 1969.
20. H. P. Gregor, J. I. Bregman, F. Gutoff, R. O. Broadley, D. E. Baldwin, and C. G. Overberger, *J. Colloid Sci.*, **6**, 20 (1951).
21. K. W. Pepper, *J. Appl. Chem.*, **1**, 124 (1951).
22. B. Chakravorty, R. N. Mukherjee, and S. Basu, *J. Membr. Sci.*, **41**, 155 (1989).
23. V. F. Wolfen, Br. Pat. 954,865 (1964).
24. M. F. Hoover and R. N. Thompson, U.S. Pat. 3,128,257 (1964).
25. W. Zhang, M. Wahlgren, and B. Sivik, *Desalination*, **72**, 263 (1989).
26. J. Kopecek and S. Sourirajan, *Ind. Eng. Chem. Process Design Dev.*, **9**, 5 (1970).
27. M. Bertholin, G. Boissier, and J. Dubios, *J. Makromol. Chem.*, **182**, 2075 (1981).
28. P. P. Wieczorek, B. N. Kolarz, and H. Galina, *Angew. Makromol. Chem.*, **126**, 39 (1984).
29. S. Detoni and D. Hadzi, *Spec. Chim. Acta*, **11**, 601 (1957).
30. E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).
31. B. N. Kolarz, P. P. Wieczorek, and M. Wojaczynska, *Angew. Makromol. Chem.*, **96**, 193 (1981).
32. H. Galina and B. N. Kolarz, *Polym. Bull.*, **2**, 235 (1980).
33. R. H. Wiley, W. K. Mathews, and K. F. O'Driscoll, *J. Macromol. Sci.*, **A1**, 503 (1967).
34. K. Dusek, in *Polymer Networks Structural and Mechanical Properties*, A. J. Chompft, Ed., Plenum Press, New York, 1971, p. 245.
35. G. Odian, Ed., in *Principles of Polymerization*, 2nd ed, Wiley-Interscience, New York, 1981, pp. 488-489.
36. D. H. Freeman and A. S. Aiyar, *Anal. Chem.*, **39**, 1141 (1967).
37. F. Martinola and A. Meyer, *Ion Exch. Membr.*, **2**, 111 (1975).

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