Photochemically Modified Thin-Film Composite Membranes. I. Acid and Ester Membranes

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SYNOPSIS

A photochemically active membrane was made by the interfacial copolymerization of 3-diazo-4-oxo-3,4-dihydro-1,6-naphthalene disulfonylchloride and naphthalene-1,3,6-trisulfonylchloride with 1,6-hexanediamine. The chemical functionality of the membrane surface was modified on irradiation of the surface of the membrane in the presence of various nucleophiles. Surface analysis techniques of attenuated total reflectance–Fourier transform infrared and scanning electron microscopy have been used to monitor the changes in the chemistry of the thin-film composite membranes. The surface functionality of the membrane was shown to affect the reverse osmosis flux and separation of various solutes. Results for membranes which have been converted to acid, and ester forms are presented. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The importance of surface chemistry in determining the separation characteristics of a membrane are well recognized.[1] However, a systematic investigation of the effect of surface functionality on the performance (solute flux and separation) of a membrane is not easy to conduct in that it is necessary to prepare a series of membranes with the same morphology but which differ only in the chemical composition of the surface. For example, the use of different monomers to vary the surface chemistry would introduce unwanted variables such as reactivity, solubility, and polymer structure differences which would not allow one to study surface phenomenon exclusively. In order to overcome this we have developed a photochemically active "standard" membrane made by incorporating a photolabile group into the thin-film composite polymer coating.[2,3] This photochemically active layer can be subsequently modified in terms of chemical functionality by irradiation with long wavelength light. The previous membranes we have described were made by precoating a polysulfone support with polyeth-yleneimine (PEI), crosslinking this polyamine coating, and then adding the photoreactive group by chemically bonding it to unreacted amine sites in the surface layer.[3] These membranes turned out to have good reverse osmosis properties, but were not entirely suitable for the study of surface effects. The PEI has a branched chain polymer structure containing tertiary amine sites which are easily protonated giving positively charged surfaces. This net positive charge outweighed any surface modifications which were attempted. To overcome this problem we have developed and describe here a new type of membrane based on the interfacial copolymerization of an aqueous diamine and an organic solution of di- and trisulfonylchlorides.

Thin-film composite membranes have been made by interfacial polymerization[4] to produce commercially viable membranes.[5,6] A wide variety of polyamide-type and other polymeric membranes have been made by modifications of this thin-film composite technique[7-10] and also as asymmetric membranes.[11] Surface analysis techniques have proven valuable in evaluating the relationship between fabrication technique and final membrane structure.[8,12] Methods used included scanning electron microscopy (SEM), energy-dispersive spectral analyzer (SEM/EDS), attenuated total reflectance–Fourier transform infrared (ATR-FTIR), and Rutherford backscattering spectroscopy.[2,3,8] In this article, a

modified version of the above fabrication methods is used to make membranes which can subsequently be modified photochemically. Membrane performance (flux and separation) and SEM and ATR-FTIR are used to evaluate and interpret the membrane behavior.

Thin film composite membranes, type MT100, MT200, and MT300, were made by the interfacial polymerization of a low-molecular mass diamine with di- and trisulfonylchlorides on the surface of a polysulfone ultrafiltration membrane. The monomers were dissolved in immiscible solvents and an interfacial polymerization technique was used similar to that used by others.[4–6] Crosslinking was controlled by the addition of various amounts of naphthalene-1,3,6-trisulfonylchloride (NTSC) to improve the strength of the film. The result was a thin coating of a polysulfonamide polymer on the surface of a support membrane.

For comparison purposes, the MT100 series membranes were fabricated with no photolabile group, as illustrated in Scheme 1. A diamine, in water, was reacted interfacially with a mixture of naphthalene-1,5-disulfonylchloride (NDSC) and (NTSC) in CCl₄, to form the polysulfonamide coating. A variety of diamines were used including: m-phenylenediamine (MPD), piperazine (PP), ethanediamine (ED), and 1,6-hexanediamine (HD).

The photoreactive MT200 and MT300 series membranes were created by substituting the light-sensitive diazoketonedisulfonylchloride (DKDSC) for the (NDSC) as illustrated in Scheme 2. MT200 and MT300 membranes were distinguished by the

relative amount of di- to trifunctional sulfonylchloride in the reaction mixture, as tabulated in Table I.

In the case of the diazoketone containing thin-film composite membranes the effect of photochemical conversion of the thin film was examined. Irradiation of the membranes with light (350 nm) photochemically transforms the diazoketone functionality. This reaction of the diazoketone moiety is similar to that previously described.[2,3] Briefly, the diazoketone undergoes a Wolff rearrangement to form a highly reactive ketene, $=C=O$. In the presence of any nucleophile, HY, the ketene reacts to form the stable $—COY$ structure. For example, photoreaction in water or alcohol solvents produces carboxylic acid or ester groups, respectively. The effect of the introduction of carboxylic acid and ester functionality to the membranes is examined.

EXPERIMENTAL

The equipment and methods used are similar to those previously described;[2,3] details are given here.

Reverse Osmosis Experiments

All membrane tests were conducted at 6000 kPa and $25 \pm 2°C$. Each feed solution was allowed to circulate at complete recycle (concentrate and permeate returned to the feed tank) for approximately 20 h before samples were taken. The membrane surface area was 1.508×10^{-3} m² and the feed flow rate was kept at 1.0 L/min. Feed salt solutions were 0.17 M and
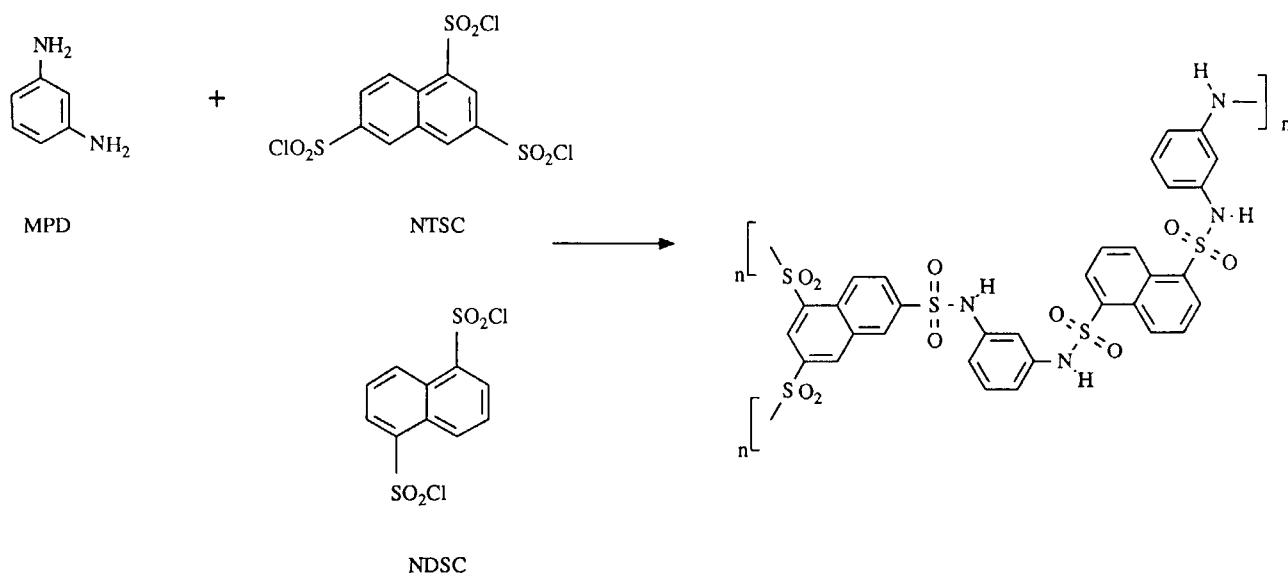
Scheme 1

Scheme 2
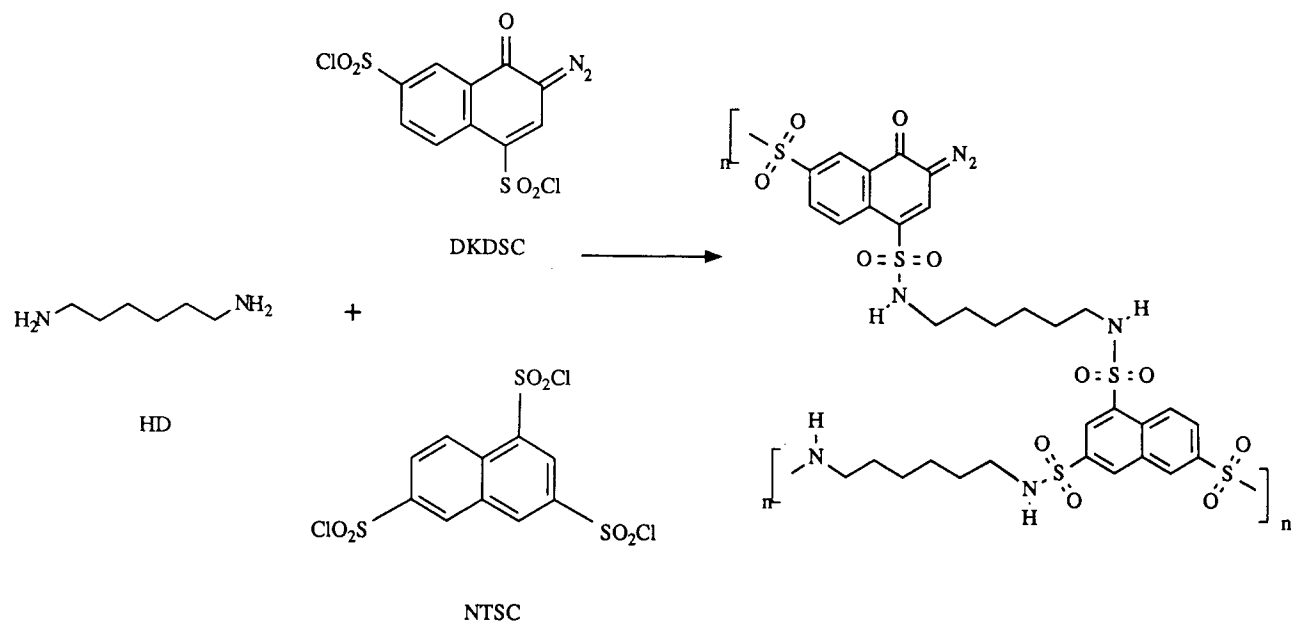
the sucrose feed concentration was 0.03 molar (1.0 mass %). All membranes were prepared and tested in duplicate. The membranes are photosensitive; all manipulations were carried out under reduced light or in the dark.

Membrane Fabrication

The base polysulfone ultrafiltration membrane used in this work was a machine-cast proprietary material. A disk of the support membrane was cut from the bulk roll and allowed to soak in water for at least 20 h prior to any treatment. The disk was subsequently soaked in a 1.0 mass % aqueous solution of the appropriate diamine for 2 h. The excess diamine solution was removed from the surface of the polysulfone base membrane using a rubber roller and the membrane was placed in a CCl_4 solution of the appropriate sulfonylchloride for 25 min and then

was allowed to air dry for 30 min. With the exception of the MT302 samples, membranes were heat treated in a convection oven at 100°C for 5 min. The exact concentrations and ratios of monomers for the different membrane types are summarized in Table I.

Photochemical Conversion of Membranes

The thin-film composite membranes containing the diazoketone grouping were of pale yellow color. The membranes produced above were soaked in water, ethanol, methanol, or isopropanol for 1.0 h and then irradiated while still contacted with this solvent in a Petri dish at 350 nm for 10 min.[2,3] During this irradiation the membranes lost the pale yellow coloration. Following photochemical treatment, the membranes were soaked in water overnight to remove any residual reagents before testing. Nonirradiated membranes, after air-drying, were similarly soaked in water overnight before testing.

Table I   Summary of Membrane Fabrication Parameters

Membrane Type	Heat Treatment (Y/N)	Monomer Mass % Ratio DKDSC/NTSC or (NDSC/NTSC)	Total Monomer Conc. (mass/vol % in CCl_4)
MT100	Y	(50/50)	0.25
MT200	Y	50/50	0.25
MT301	Y	95/5	0.25
MT302	N	95/5	0.25

Chemical Synthesis

Naphthalene-1,3,6-trisulfonylchloride (NTSC) was obtained from trisulfonic acid trisodium salt (20 g) (Fluka Chemical Corp.) by reaction with PCl_5 (40 g) using the method of Ceasar.[13] The product was a white powder *mp* 191–194°C. Mass spectrum *m/e* (relative intensity) 422,424,426,428 (M^+) Cl isotope pattern, 125 (100). ^1H nuclear magnetic resonance (NMR) ($CDCl_3$) δ 8.55 (*d*, 1), δ 8.98 (*s*, 1), δ 9.03 (*s*, 1), δ 9.14 (*s*, 1), δ 9.18 (*d*, 1).

3-Diazo-4-oxo-3,4-dihydro-1,6-naphthalene disulfonylchloride (DKDSC) was prepared from 1-naphthylamine-7-sulfonic acid (FLUKA) via a 5 step synthesis:

1. 1-Naphthylamine-4,7-Disulfonic Acid. 1-Naphthylamine-7-sulfonic acid (4.8 g), 98% H_2SO_4 (15.5 g), and SO_3 (26 g) were reacted using the I.G. (Leverkusen) process[14] (yield 7 g). ^1H NMR (D_2O) δ 6.3 (*d*, 1), δ 7.5 (*d*, 1), δ 7.6 (*d*, 1), δ 8.0 (*s*, 1), δ 8.3 (*d*, 1).
2. 1-Naphthol-4,7-Disulfonic Acid. 1-Naphthylamine-4,7-disulfonic acid (2 g) and 20 mL of 40% sodium bisulfite solution were reacted using the method of Bucherer[15] (yield 1.1 g). ^1H NMR (D_2O) δ 6.9 (*d*, 1), δ 7.9 (*d*, 1), δ 8.0 (*s*, 1), δ 8.6 (*d*, 1), δ 8.7 (*s*, 1).
3. 2-Aminohydrochloride-1-naphthol-4,7-Disulfonic Acid. Naphthol-4,7-disulfonic acid (20 g) was coupled with benzene diazonium chloride and reduced to form the α amino naphthol.[16] ^1H NMR (D_2O/NaOD) δ 7.4 (*d*, 1), δ 7.6 (*s*, 1), δ 8.2 (*d*, 1), δ 8.4 (*s*, 1).
4. 2-Diazo-1-naphthol-4,7-Disulfonic Acid. 2-Aminohydrochloride-1-naphthol-4,7-disulfonic acid (32 g), $CuSO_4$ (0.2 g), and $NaNO_2$ (20 g) in 125 mL H_2O were used in the diazotization reaction as similarly described by Woodward[17] (yield 19 g). ^1H NMR (D_2O) δ 7.9 (*s*, 1), δ 8.1 (*d*, 1), δ 8.4 (*d*, 1), δ 8.6 (*s*, 1).
5. 3-Diazo-4-oxo-3,4-dihydro-1,6-naphthalene Disulfonyl Chloride. Diazoketone-4,7-disulfonic acid (10 g) was suspended in CH_2Cl_2 (13 mL) and $SOCl_2$ (17 mL) with stirring. DMF (17 mL) was added slowly and the reaction stirred at 20°C for 15 h. The solution was added dropwise to ice water (50 mL) keeping the temperature below 10°C while stirring vigorously. The product precipitated initially as a paste and on stirring formed a bright yellow powder. The product was collected *in vacuo*, washed with ice-cold wa-

ter and dried under vacuum (yield 4.5 g). Mass spectrum *m/e* (relative intensity) 366,368,370 (M^+) Cl isotope pattern, 239 (100), 303 (90). ^1H NMR ($CDCl_3$) δ 8.35 (*d*, 1), δ 8.45 (*s*, 1), δ 8.65 (*d*, 1), δ 9.05 (*s*, 1). IR KBr 2160 cm^{-1} ($C-N_2$), 1650 cm^{-1} ($C=O$).

RESULTS AND DISCUSSION

All of the results presented were obtained using a minimum of two membrane samples with variations in flux and separation of approximately ±10% and ±3%, respectively. Although the reproducibility between membranes of the same batch was good, the reproducibility between batches was somewhat lower due to the reuse of the CCl_4 solutions of DKDSC in order to conserve this material. As a result of this variation, standard nonirradiated membranes containing the diazoketone were included in every batch of membranes fabricated and tested (referred to as DK membranes) so the results for converted membranes could be compared with the corresponding nonirradiated membranes.

Pure Water and Solution Permeabilities

One common factor among all the different polysulfonamide membranes was compaction of the surface layer by pure water and further compaction during solution (water plus solute) permeation experiments. Initially, at installation, the membranes had a very high pure water flux, on the order of 22 × 10^{-3} kg/m^2 s, which leveled off after 3 h to about 14 × 10^{-3} kg/m^2 s. When a solute was introduced, the membrane compacted further, and after approximately 20 h reached an equilibrium solution flux. These fluxes were on the order of 6 × 10^{-3} kg/m^2 s and usually varied for the solutes in the order: NaCl > $MgCl_2$ > Na_2SO_4 > $MgSO_4$ > sucrose. Therefore, for each solute a different pure water flux was observed, which remained constant for that solute. For some membranes the testing was conducted in the order: PRA-PWI-PRA-PWF, where PRA, PWI, and PWF are solution flux of A, pure water initial flux, and pure water final flux, respectively. For example, membrane MT301-25 when tested with a 0.17*M* solution of Na_2SO_4 had an initial pure water flux of 5.6 × 10^{-3} kg/m^2 s, a solution flux of 4.4 × 10^{-3} kg/m^2 s, and a final pure water flux of 5.5 × 10^{-3} kg/m^2 s. After a week with no pressure, the pure water flux never returned to the levels at

Table II   NaCl Reverse Osmosis Performance Characteristics for MT100-302 Membranes[a]

Membrane Type	Flux $(kg/m^2 s, \times 10^3)$	Separation (%)
MT100	0.6	36
MT200	3.7	30
MT301	10.0	39
MT302	7.4	32

[a] Average of two or more membrane samples. NaCl concentration $0.17M$. Tested at 6000 kPa with temperature at $25 \pm 2°C$. Fluxes corrected to 25°C.

installation. These compaction results are interpreted based on SEMs, discussed later.

In this section the results for three different types of membranes are discussed.

MT100 Membranes

Several membranes were produced as outlined in Table I and Scheme 1 using the various diamines shown. Piperazine and ethanediamine were rejected due to poor reverse osmosis performance. MPD produced the best membranes but had to be rejected due to photochemical deactivation of the diazoketone. Photoactivity of the diazoketone and reasonable RO properties made 1,6-hexanediamine the choice for MT200 and MT300 membrane fabrication.

MT200 Membranes

A number of membranes were prepared as outlined in Table I using HD as the diamine. As can be seen from the data in Table II, the incorporation of DKDSC into the membrane in place of NDSC has

a remarkable effect on solution flux. The flux is increased by almost an order of magnitude with only a 15% loss in separation. Increasing the ratio of DKDSC to NTSC present in the membrane carries this effect still further. The reason for the improvement in properties of the membrane with the substitution of DKDSC for NDSC is not known. However, in all our research, a membrane containing the diazoketone functional group has better flux and separation than the nonphotoreactive analog.

Some of these membranes were converted to acid or ethyl and methyl ester forms by irradiation in the appropriate medium. The reverse osmosis performance for various solutes is summarized in Table III.

Some unexpected differences in separation and flux of the membranes after irradiation and conversion of the diazoketone functions to either carboxylic acid or ester functions were observed. There is no difference in the order of separation of the solutes observed with the irradiated membranes compared with the DK membranes. The acid membranes have fluxes 30% lower than the corresponding diazoketone membranes and separations which are approximately 15% higher. There is no evidence for the expected enhancement of the hydrophilicity of the acid membrane surface. For the ester membranes the diazo group is replaced with an ester group which should be somewhat more hydrophobic. However, for the ester membranes, the solution flux is actually 80% greater than for the diazoketone membrane; the opposite expected for a more hydrophobic surface. The separation for the salts is 1 to 10% lower for the ester membranes than for the DK membranes while for sucrose the separation is 2 to 9% higher.

The results obtained suggest that the effect of the photochemical conversion was small or negligible.

Table III   Reverse Osmosis Performance Characteristics for Type MT200 DK, Ester, and Acid-Modified Membranes[a]

Membrane	Solute (Flux Sep %)									
	NaCl		MgCl$_2$		Na$_2$SO$_4$		MgSO$_4$		Sucrose	
DK	9.2	22	8.8	32	8.3	53	7.6	59	5.9	67
Acid	6.1	34	5.9	45	5.7	68	5.2	73	4.2	81
DK	5.0	34	4.8	54	4.6	60	4.4	78	4.6	71
Ethyl ester	8.7	24	8.5	42	8.1	54	7.7	72	8.1	73
Methyl ester	9.0	24	8.7	44	8.5	59	8.1	75	8.8	80

[a] Average of two or more membrane samples. Salts at $0.17M$ and sucrose at $0.03M$. Tested at 6000 kPa with temperature at $25 \pm 2°C$. Fluxes corrected to 25°C. Flux in $kg/m^2 s \times 10^3$.
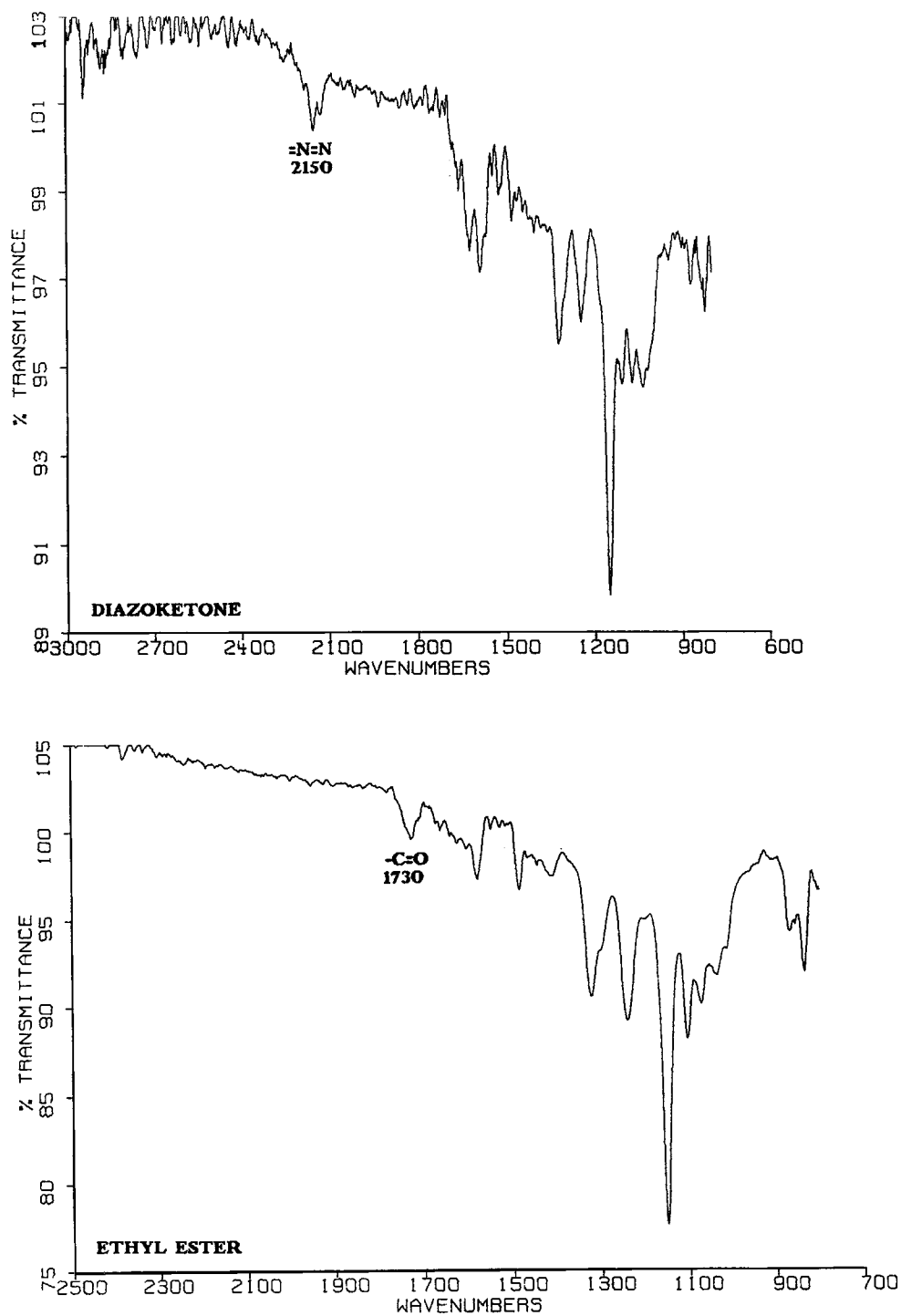
Figure 1   ATR-FTIR spectra for MT302 membranes using 45° Ge crystal and reflectance attachment of (a) DK membrane with diazo peak at 2150 cm^{-1} and (b) ethylester membrane with carbonyl peak at 1730 cm^{-1}.

Analysis of the surface, before irradiation, by ATR-FTIR failed to detect the presence of diazo absorption bands at about 2160 cm^{-1} on the membrane surface; this absorption was clearly visible for the DK membranes in previous studies.[2,3] The diazoketone functionality may have been destroyed dur-

ing heat treatment or possibly the surface concentration of the photolabile group was too low to have any real effect on the surface chemistry.

MT300 Membranes

To resolve the problems discussed above, the ratio of DKDSC to NTSC was increased to 95 : 5 by mass in the CCl$_4$ solution and diazoketone membranes were made with and without subsequent heat treatments. Examination of the surface of these membranes by ATR-FTIR showed that detectable quantities of the diazoketone were being incorporated into the thin film with the spectra of the membranes exhibiting the characteristic band at about 2150 cm^{-1} [Fig. 1(a)]. As can be seen from the data given in Table II, increasing the proportion of diazoketone present in the thin-film layer, increases the flux by a factor of 3 and the separation of NaCl by 15% over the membranes with a 50 : 50 ratio. The effect of eliminating the heat-treatment step in the preparation of these membranes also was examined. Data in Table I illustrate that elimination of this step with the 5% crosslinked membranes results in a 30% loss in flux and a 15% loss in separation. However, as there is a possibility that heat treatment may destroy even some diazo groups on the membrane surface the somewhat lower performance of the non-heat-treated membranes was chosen for subsequent work. Although the separation of some solutes may be regarded as being quite low, the large difference in separation between solutes is ideal for observing the changes in performance of the various modified membranes.

Photochemical Modification of MT302 Membranes

A series of membranes was irradiated in contact with water, methanol, ethanol, or n-butanol to form carboxylic acid, methylester, ethylester, or n-butyl ester membranes, respectively. A control experiment, where the diazoketone membrane was soaked in ethanol but not irradiated, was conducted. The reverse osmosis results for these membranes are presented in Table IV.

The photochemical modification of the membranes was followed by ATR-FTIR spectroscopy. For the ethylester membranes the diazo peak at 2150 cm^{-1} attributed to the diazo function in the starting membrane [Fig. 1(a)] disappears and a new peak is observed at 1730 cm^{-1} [Fig. 1(b)] typical of ester carbonyl absorptions. Clearly the photochemical surface modification is occurring with these membranes.

The effect of the acid conversion can be seen in Figure 2. For the acid membranes the solution flux is enhanced by approximately 25% compared with DK membranes which suggests that the surface has become more hydrophilic. At the same time, the negatively charged carboxylate group rejects solute by Donnan exclusion, which enhances, for all solutes, the solute–water separations to values above the diazoketone and ester membranes. The lines joining the data points in Figure 2 are not meant to imply a continuum of expected values; they are merely an aid in viewing the changes in the data with solute. Plotting flux and separation versus solute size, diffusivity, viscosity, and other physicochemical parameters did not prove enlightening.

Table IV   Reverse Osmosis Performance Characteristics for Type MT300 DK, Ester, and Acid-Modified Membranes[a]

Membrane	Solute (Flux Sep %)									
	NaCl		MgCl$_2$		Na$_2$SO$_4$		MgSO$_4$		Sucrose	
DK	7.4	32	6.4	49	6.3	72	6.3	76	3.9	90
Acid	8.8	68	7.9	80	8.1	94	8.1	95	7.0	97
DK	11.0	30	9.2	44	8.5	69	7.4	73	5.5	92
EtOH soak DK	15.1	28	13.3	42	12.5	70	10.9	78	6.3	92
Methyl ester	5.9	43	5.3	52	6.1	86	6.4	87	4.2	87
Ethyl ester	5.7	45	5.2	55	5.3	82	5.5	88	3.9	90
n-Butyl ester	6.3	41	5.5	53	5.7	79	5.7	82	4.6	86

[a] Average of two or more membrane samples. Salts at 0.17M and sucrose at 0.03M. Tested at 6000 kPa with temperature at 25 ± 2°C. Fluxes corrected to 25°C. Flux in kg/m^2 s × 10^3.
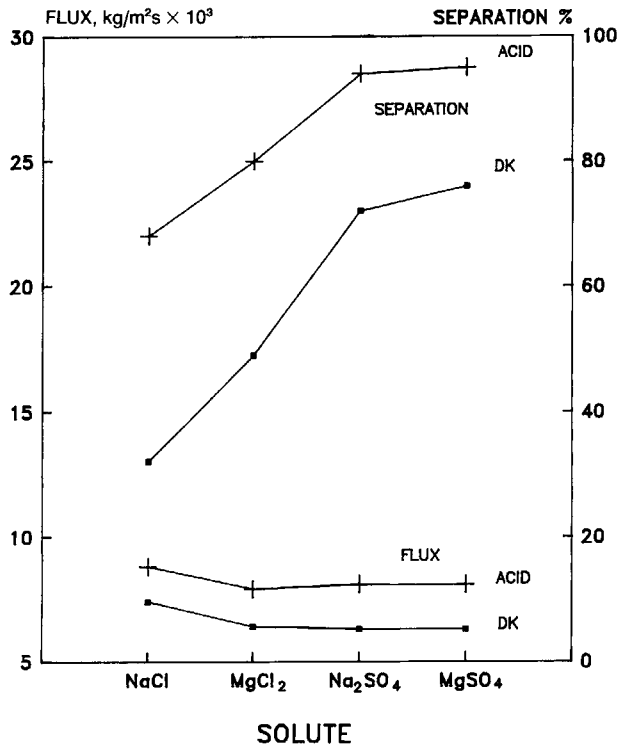
Figure 2 Reverse osmosis flux and separation for different solutes for MT302 DK and acid modified membranes.

membrane. This apparent discrepancy is not presently understood.

The control experiment of soaking the DK mem-

To further study the membrane surface conversion to acid form an RO pH profile was performed as presented in Figure 3. The pH of the NaCl test solution was cycled back and forth from acidic to basic conditions several times using HCl and NaOH, respectively. The separation for DK and acid membranes increased with increasing pH suggesting both have negative charge. The increase in separation with pH is greater (steeper slope) for the acid membrane due to a higher surface charge. The charge on the diazoketone membrane may arise from hydrolyzed $-SO_2Cl$ polymer terminae whereas the acid membranes have the additional carboxylate groups. The NaCl solution flux profile in Figure 3 clearly shows a titration-type curve for the acid membrane representing the conversion of surface carboxylic acid groups to carboxylate anions. This effect cannot be seen for the DK membranes which further supports the expected change in performance with the change in surface chemistry to a negatively charged membrane. The apparent pK_a of the membrane (ca. 6.5) appears high for carboxylic acid groups (pK_a about 4.5). Currently, attempts are being made to measure the pK_a (and the charge density) of the
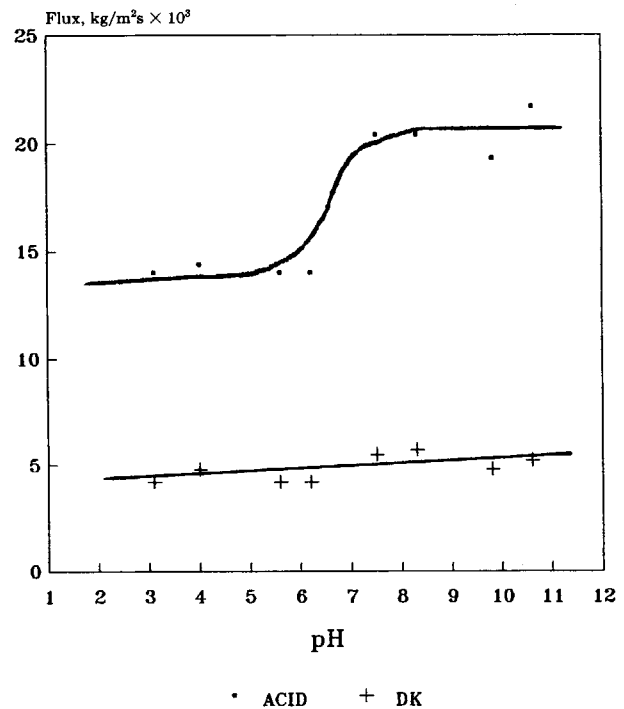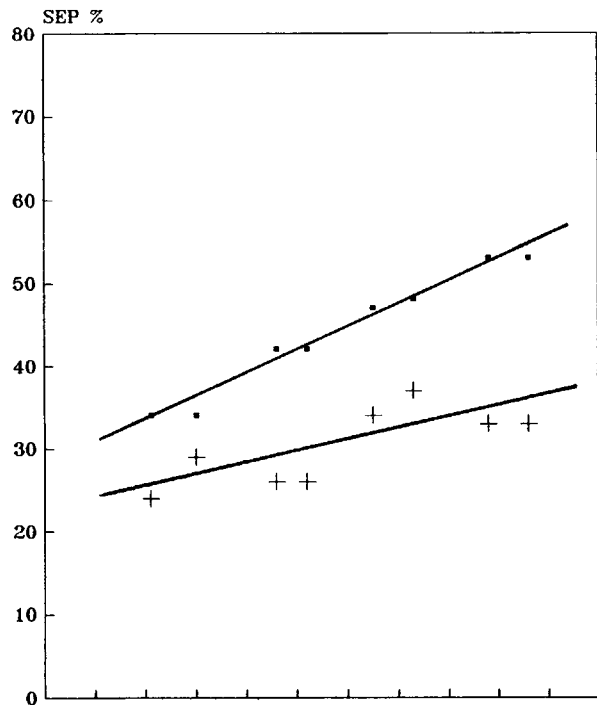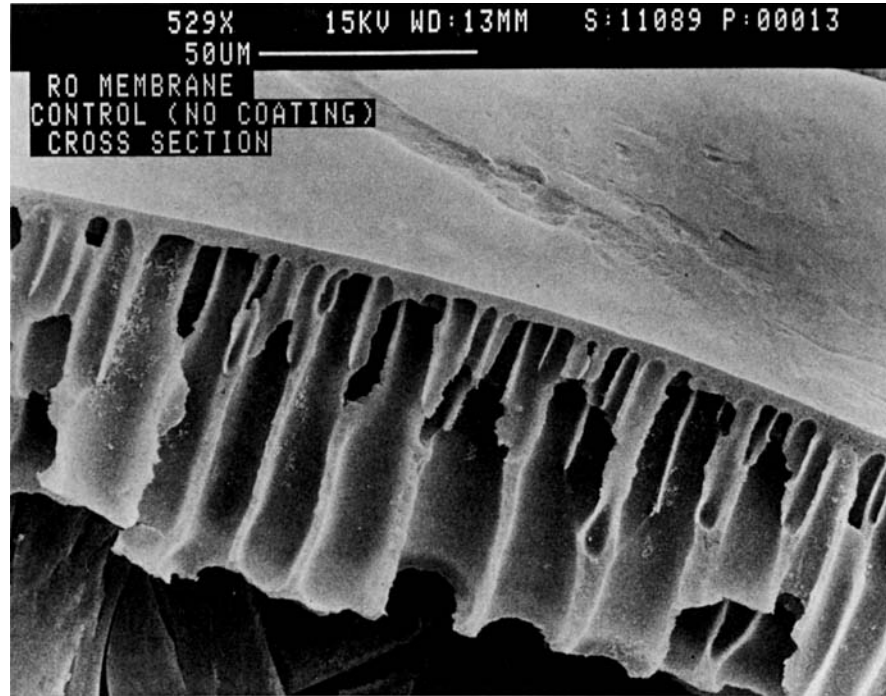

Figure 3 NaCl separation vs. pH for MT302 DK and acid modified membranes.
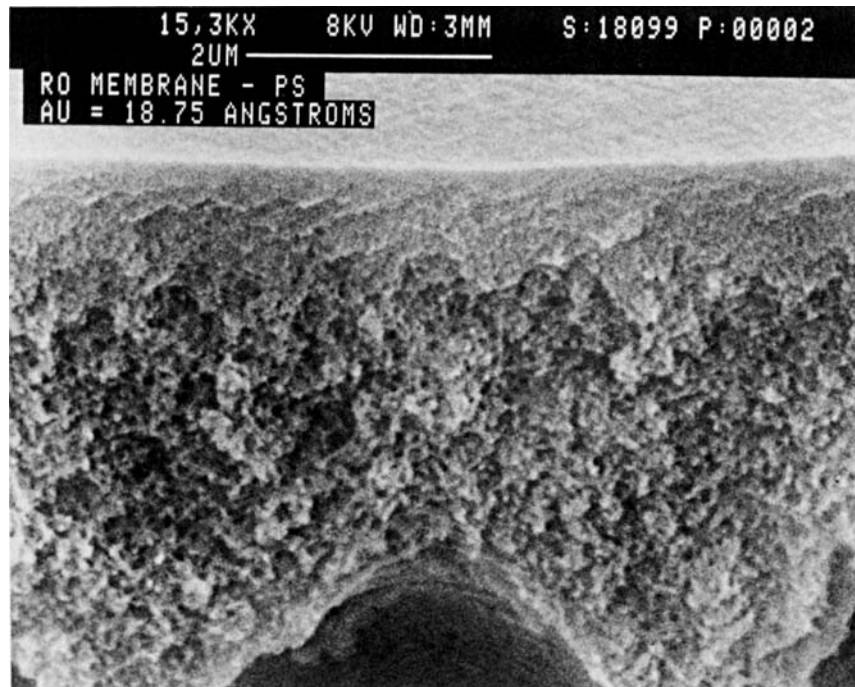
(a)

(b)

Figure 4 SEM of the uncoated polysulfone support membrane. (a) Tilt cross-section of the membrane at low magnification; (b) higher magnification cross-section at the membrane surface.

brane in ethanol in the absence of light has a substantial effect on the membrane, increasing the flux by 40% without changing the separation. Ethanol appears to cause the membrane to swell. Despite these irreversible changes to the membrane which

are observed for the control experiment, the opposite effect is observed with irradiation in the presence of ethanol. The ester converted membranes have, on average, a 35% lower solution flux than the corresponding diazoketone membranes (Table IV).
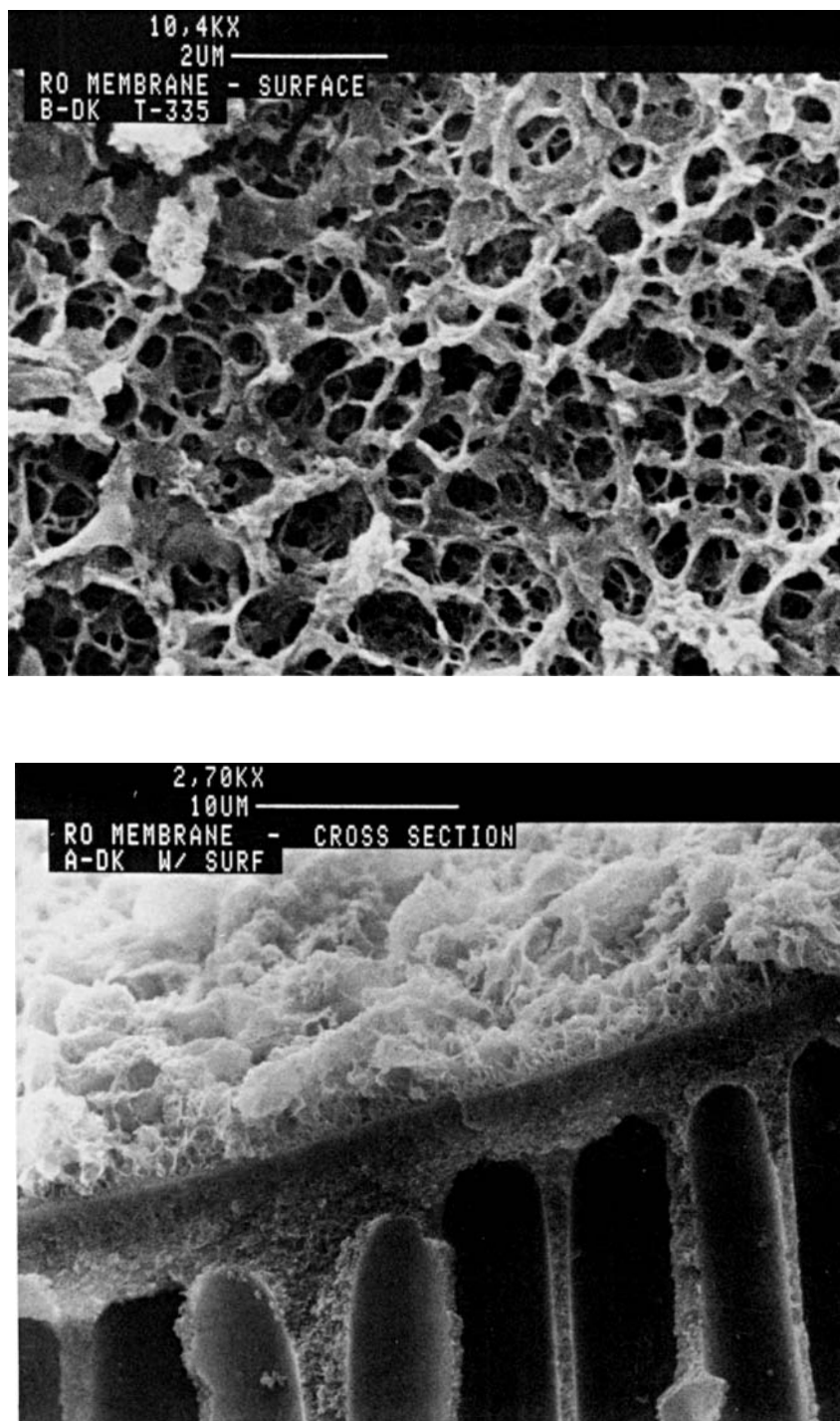

Figure 5   Cross section and surface SEMs of MT302 DK membrane.

This result clearly confirms that the photochemistry is working not only at the surface of the thin-film layer, but also at the working level where the separation characteristics are determined. This effect of converting the diazoketone groups to esters outweighs or eliminates the swelling effect. Conversion of the membrane surface to ester form with straight chain hydrocarbon-like functionality would seem, as expected, to have produced more hydrophobic membranes which exhibit lower solution flux and somewhat higher solute separation.

The variation in performance among the esters is not completely clear. One would expect that as the hydrocarbon chain of the ester is made longer the flux should continue to decrease. This trend can not be seen within experimental error for the esters studied in this work. Further work is needed with even longer chain and branched chain esters to resolve this effect.

SEM Characterization of MT300 Membranes

For comparison, SEMs of the nascent polysulfone membrane are presented in Figure 4. Figure 4(a) is a low magnification tilted cross-section showing, from bottom up, part of the nonwoven polyester support, the finger-like voids in the polysulfone, a relatively dense skin of polysulfone near the surface, and the smooth surface of the membrane. Figure

4(b) is a higher magnification cross-section of the skin, previously determined[3] to have a molecular mass cutoff of 200,000, which is observed to be quite uniform.

The SEMs of DK, acid, and ester membranes were reasonably reproducible. Typically, the DK membranes had thick honeycomb-like or cellular structures on the surface coating (Fig. 5). Average thicknesses were on the order of 1500 nm and surface openings ranged from 50 to 1000 nm in diameter. These openings must lead to a denser substructure which is necessary to account for the RO properties of the membrane. The compaction of this thick surface layer in the RO system accounts for the decrease in flux observed at installation. Membranes photochemically modified to the acid form and control membranes (DK membranes soaked in EtOH but not irradiated) had structures similar to the parent DK membrane with no discernible differences. Recent work has suggested that the formation of the cellular structure is due to the formation of vesicles in the aqueous diamine and surfactant solution; results will be published separately.

Samples irradiated in alcohol solutions tended to have smoother surfaces, that is the edges of the cells have been rounded off and reduced in number, as presented in Figure 6 for an ethylester membrane. Since the EtOH soaked control membranes were similar in structure to the DK and acid membranes
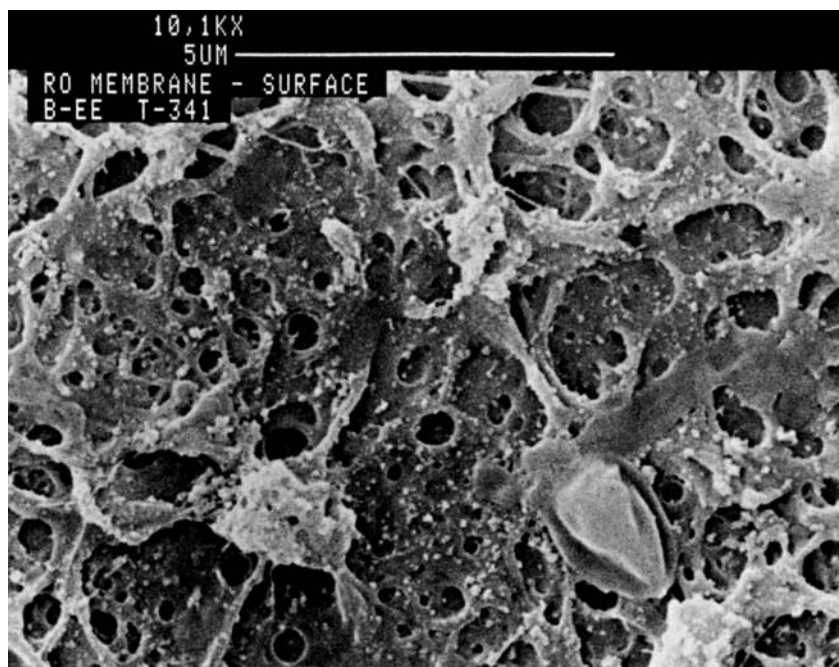

Figure 6   SEM of MT302 ethylester-converted membrane.

the presence of both EtOH and photochemical reaction are necessary to change the surface structure. This change in structure is due either to a swelling and subsequent collapse of the honeycomb structure or a partial dissolving of the polymer. Top layer openings were of the same size as for the DK membrane but were reduced in number while surface thicknesses were reduced to about 1000 nm. In all cases, the interfacial polymer structure of the membrane was not radically altered by the nucleophiles or irradiation procedure yet marked changes in RO performance were observed as discussed above.

CONCLUSIONS

We have presented a method for fabricating reverse osmosis membranes which can be modified by a photochemical technique. The photochemistry and hence the membrane performance work best with a large concentration of the photoreactive monomer (a diazoketone disulfonylchloride) in CCl_4 during the interfacial polymerization procedure and without subsequent heat treatment. The membranes were found to require approximately 20 h to reach steady state with each solute. Conversion to carboxylic acid functionality by irradiation in water produced a negatively charged membrane which exhibited pH dependence. This acid membrane has a more hydrophilic surface, thus enhancing solution flux and separation. Irradiation of the membranes in alcohols to form ester membranes produced a more hydrophobic surface causing solution flux to be depressed which in turn enhanced salt rejection. The diazoketone membrane (before photochemical reaction), the membrane converted to acid form photochemically, and the alcohol-soaked control membrane had an open cellular surface structure. Membranes converted to ester form had surfaces that were smoother due to either a swelling and collapse of the structure or a partial dissolving effect during the irradiation. Surface analysis techniques of ATR-FTIR and SEM proved useful to monitor the physicochemical nature of the membranes.

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