

# Photochemically Modified Thin-Film Composite Membranes. II. Bromoethyl Ester, Dioxolan, and Hydroxyethyl Ester Membranes

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## SYNOPSIS

A photochemically active thin-film composite membrane was made by the interfacial copolymerization of a mixture of 3-diazo-4-oxo-3,4-dihydro-1,6-naphthalene disulfonylchloride and naphthalene-1,3,6-trisulfonylchloride in CCl<sub>4</sub> with aqueous 1,6-hexanediamine on the surface of a polysulfone ultrafiltration membrane. The chemical functionality of the resulting polysulfonamide membrane surface was modified via a photochemical reaction in the presence of various nucleophiles to form membranes containing bromoethyl ester, dioxolan, and hydroxyethyl ester functionality. Surface analysis techniques of attenuated total reflectance-FTIR, scanning electron microscopy (SEM), energy disperse spectral analyzer (SEM/EDS), and electron spectroscopy (ESCA) were used to confirm the changes in the chemistry of the thin-film composite membranes. Changes in chemistry, on irradiation, were also examined with model compounds. The reverse osmosis flux and separation of various solutes with these membranes are reported and discussed in terms of the photochemical modifications of the membrane surface. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The separation properties of a reverse osmosis membrane are determined in large measure by the chemical interactions of the solute/solvent with the active layer of the membrane.<sup>1</sup> In this regard thin-film composite membranes are attractive in that, in principle, the chemical properties of the thin film can be optimized to suit a particular application while leaving the base support membrane unchanged.

One difficulty in systematically varying the chemical functionality of the thin-film layer is that, in general, this involves the preparation of a variety of different monomers and subsequent interfacial deposition as thin films on the surface of a support membrane. Not only can this be a time-consuming process but it can also be difficult to eliminate physical effects introduced during the polymerization

step. We have sought to overcome these difficulties by developing a novel composite membrane in which a photochemically active group is incorporated into the thin-film polymer.<sup>2-4</sup> The photolabile component in the thin-film polymer can be converted on irradiation with long wavelength light into a wide range of different functionalities; in principle, without significant change in the supporting thin-film polymer. This technique of photofunctionalization, and also photocrosslinking, has been used recently to modify ABS pervaporation membranes.<sup>5</sup>

Our previous studies have discussed the formation of a thin-film polymer containing a diazoketone grouping<sup>6,7</sup> that can be formed on interfacial polymerization of 3-diazo-4-oxo-3,4-dihydro-1,6-disulfonylchloride (a diazoketone disulfonylchloride; DKDSC) with 1,6-hexanediamine on the surface of a polysulfone (PS) ultrafiltration membrane.<sup>4</sup> The basic thin-film forming technique parallels that developed by Cadotte and others (e.g., Refs. 8 and 9). The effect of photochemical modification of the thin film to carboxylate and ester functionalities has been described in Part I.<sup>4</sup> Here, we describe an expansion

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of this work to include an examination of the properties and subsequent chemical modifications of membranes containing esters of 2-bromoethanol. Our purpose in exploring these membranes was to form positively charged thin films by subsequently displacing the bromine with a suitable amine, Scheme 1. As described below, this route did not yield the cationic membranes but instead gave rise to some unusual chemical transformations and membranes with useful properties.

## EXPERIMENTAL

This section briefly outlines the membrane fabrication and testing methods, surface analysis, and chemical synthesis.

### Reverse Osmosis Experiments

All membrane tests were conducted at 6000 kPa and  $25 \pm 2^\circ\text{C}$  using the apparatus described previously.<sup>2</sup> Fluxes were corrected to  $25^\circ\text{C}$  using the viscosity and density of water.<sup>10</sup> The feed solution was circulated at complete recycle (concentrate and permeate were returned to the feed tank) for approximately 20 h before data were obtained. The membrane surface area was  $1.508 \times 10^{-3} \text{ m}^2$ , the feed flow rate was 1.0 L/min, and the feed concentration was 0.17 M for the solutes NaCl,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{MgSO}_4$ . Feed and permeate concentrations were determined at  $25^\circ\text{C}$  by a YSI Model 31 conductivity meter calibrated for each salt. Results presented are for a minimum of two membrane samples with variations in flux and separation of approximately  $\pm 10\%$  and  $\pm 3\%$ , respectively. Controls (nonirradiated membranes and membranes soaked in the various solvent solutions and not irradiated) were included and tested for comparison.

### Membrane Fabrication

The general procedure used to fabricate the diazo-ketone-containing membranes (DK) (prepared in at least duplicate) has been previously reported.<sup>4</sup> The diamine used in the aqueous step was 1,6-hex-

anediamine. The organic phase consisted of a mixture of DKDSC and naphthalene-1,3,6-trisulfonylchloride (NTSC) monomers in a 95:5 mass % ratio at a total organic phase concentration of 0.25 mass/vol % in  $\text{CCl}_4$ . Interfacial polymerization was allowed to continue for 25 min, then the membranes were removed from  $\text{CCl}_4$ , and allowed to air dry for 30 min at room temperature. DK membranes, to be subsequently modified, were soaked in ethanol for 5 min to help remove any residual monomers or water and air dried for 5 min. No heat treatment process was used with the membranes.

### Conversion to Ester Derivative

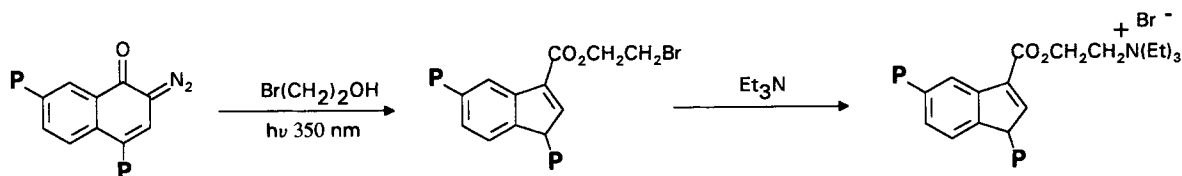
The membranes prepared as above were soaked in the appropriate solution containing the desired alcohol for 30 min at room temperature and then irradiated at 350 nm for 10 min. The resulting membranes were washed with ethanol to remove any residual reactant. For the bromoethyl ester membranes, the reactant solution was 10, 20, or 30 vol % 2-bromoethanol in dry diethylether. For the directly produced hydroxyethyl ester membranes, the reactant solution was 10 vol % ethylene glycol in dry diethylether.

### Conversion of Bromoethyl Ester Derivative to a Dioxolan

The bromoethyl ester containing membranes were treated with triethylamine (20 vol % in ethanol) for 1 h at room temperature. Following this treatment the membranes were washed and stored in water before testing.

### Surface Analysis

The following instruments were used in the membrane surface analysis: attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Biorad-Digilab FTS-40), scanning electron microscopy with energy dispersive analyzer (SEM/EDS) (Perkin-Elmer PHI 5100 ESCA), and scanning electron microscopy (SEM) (Cambridge Instruments S240).



Scheme 1

## Materials and Chemical Synthesis

5-Diazo-5,6-dihydro-6-oxo-1-naphthalene-*N,N*-diethylsulfonamide, **1**, was obtained by reaction of 5-diazo-5,6-dihydro-6-oxo-1-naphthalenesulfonyl chloride (Fluka) with diethylamine, according to the method described elsewhere.<sup>2</sup>

3*H*-indene-1-carboxylic acid 3'-bromoethyl ester, 4-[(diethylamino)sulfonyl], **2**, a solution of **1** (0.1 g; 0.33 mmol) and 2-bromoethanol (1 mL; 14 mmol) in 100 mL of diethyl ether, was irradiated at 350 nm for 1 h. The solution was extracted with 4 × 50 mL of water and dried over anhydrous sodium sulfate. Removal of ether under vacuum gave pure **2**. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ1.1 CH<sub>3</sub> (*t*, 6), 3.3 CH<sub>2</sub> (*q*, 4), 3.6 CH<sub>2</sub>-ester (*t*, 2), 3.9 CH<sub>2</sub> (*s*, 2), 4.6 CH<sub>2</sub>-ester (*t*, 2), 7.5 H<sub>6</sub> (*t*, 1), 7.7 H<sub>2</sub> (*s*, 1), 7.8 H<sub>7</sub> (*d*, 1), and 8.3 H<sub>5</sub> (*d*, 1). Mass spectrum *m/z* (relative intensity) 401 (85), 386,388 (70), 265,267 (70), and 72 (100).

1*H*-indene-1-(1',3'-dioxolan-2'-ylidene), 4-[(diethylamino)sulfonyl], **3**, a solution of **2** (0.05 g; 0.1 mmol) and triethylamine (1 mL) in 95% ethanol (20 mL), was stirred at room temperature for 1 h. The solvent and excess triethylamine were removed under vacuum. Addition of diethyl ether precipitated any impurities that were removed by filtration. Addition of *n*-hexane and cooling formed crystals of pure **3**. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ1.1 CH<sub>3</sub> (*t*, 6), 3.3 CH<sub>2</sub> (*q*, 4), 4.5 CH<sub>2</sub>-dioxolan (*t*, 2), 4.6 CH<sub>2</sub>-dioxolan (*t*, 2), 7.0 H<sub>3</sub> (*d*, 1), 7.1 H<sub>2</sub> (*d*, 1), 7.2 H<sub>6</sub> (*t*, 1), 7.6 H<sub>7</sub> (*d*, 1), and 7.9 H<sub>5</sub> (*d*, 1). Mass spectrum: *m/z* (relative intensity), 321 (20), 249 (10), 186 (100), 113 (25), and 72 (100).

3*H*-indene-1-carboxylic acid hydroxyethyl ester, 4-[(diethylamino)sulfonyl], **4**, a solution of **1** (0.1 g; 0.33 mmol) and ethylene glycol (15 mL; 0.27 mol) in 85 mL of diethyl ether, was irradiated at 350 nm for 2 h. Excess ethylene glycol was extracted with 3 × 100 mL of water and the organic phase was dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave pure **4**. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ1.0 CH<sub>3</sub> (*t*, 6), 3.25 CH<sub>2</sub> (*q*, 4), 3.75 H<sub>3</sub> (*s*, 2), 3.9 CH<sub>2</sub>-ester (*t*, 2), 4.4 CH<sub>2</sub>-ester (*t*, 2), 7.4 H<sub>6</sub> (*t*, 1), 7.5 H<sub>2</sub> (*s*, 1), 7.65 H<sub>7</sub> (*d*, 1), and 8.2 H<sub>5</sub> (*d*, 1). Mass spectrum: *m/z* (relative intensity), 339 (45), 324 (30), 209 (30), 203 (60), 167 (30), 115 (30), 86 (30), and 72 (100).

## RESULTS AND DISCUSSION

In this section the reverse osmosis and surface analysis results for two different types of membranes are discussed. The first section presents results for the

bromoethyl ester membranes. The second section deals with the membranes obtained on amine treatment of these bromoethyl ester membranes.

### Bromoethyl Ester Membranes

The thin-film composite membranes used in this work were prepared by the interfacial polymerization of 1,6-hexanediamine with DKDSC as described above (SEMs of the polysulfone support and the coated DK and ethyl ester membranes were presented in Part I<sup>4</sup>). The reverse osmosis properties of the starting diazoketone containing membranes were measured so as to provide a control experiment for comparison to subsequent treatments (in Table I as DIAZOKETONE). The thickness of the coating layer of these DK membranes was examined by SEM and found to be approximately 1500 nm.

The photoreactions of the DK membranes with 2-bromoethanol were examined. Preliminary experiments were carried out in which the diazoketone precursor membranes were irradiated in the presence of 2-bromoethanol as a solvent. Under these conditions the 2-bromoethanol caused severe degradation of the membrane with clearly visible erosion of the surface coating.

In order to mitigate the degradation of the membranes caused by 2-bromoethanol the effect of using diethyl ether solutions of this alcohol was examined. The second entry in Table I presents the properties of a coated membrane after contact (soaking without irradiation) with a 20% solution of 2-bromoethanol in diethylether in the dark. Compared to the diazoketone membranes, the performance of these membranes after this treatment is not substantially different. The measured solute separations do not change significantly, however, a small increase in the measured flux (ca. 15%) was observed. This flux increase is attributed to a swelling of the coating layer in the presence of the bromoethanol. A similar effect was seen on soaking the same starting membranes in other alcohols.<sup>4</sup> Scanning electron micrograph examination of the thin-films of these dark soaked membranes indicated that there was no detectable change in the thickness or nature of the coatings.

### Photochemical Modification

The thin-film composite membranes containing the diazoketone moiety were irradiated with light of 350 nm in the presence of ether solutions containing 10–30% of 2-bromoethanol. Examination of the ATR-FTIR spectra of the membranes showed that this irradiation caused the loss of the bands at ca.

**Table I** Reverse Osmosis Performance Characteristics for Control and Modified Membranes<sup>a</sup>

Membrane	Solute (Flux Sep%)							
	NaCl		MgCl <sub>2</sub>		Na <sub>2</sub> SO <sub>4</sub>		MgSO <sub>4</sub>	
DIAZOKETONE	11.0	30	9.2	44	8.5	69	7.4	73
BrEtOH/Et <sub>2</sub> O SOAK <sup>b</sup>	12.7	25	10.1	45	9.6	71	9.6	75
BROMOESTER <sup>c</sup>	5.5	24	4.8	33	4.8	65	5.0	66
DIOXOLAN <sup>d</sup>	0.3	88	0.3	95	0.3	98	0.3	97

<sup>a</sup> Average of two or more membrane samples. Salts at 0.17M at pH approx. 6. Tested at 6000 kPa with temperature at 25 ± 2°C. Fluxes corrected to 25°C. Flux in kg/m<sup>2</sup> s, × 10<sup>3</sup>.

<sup>b</sup> Control DK membrane soaked in a 20% 2-bromoethanol in diethylether solution for 30 min.

<sup>c</sup> DK membrane irradiated at 350 nm in a 20% 2-bromoethanol in diethylether solution.

<sup>d</sup> Bromoethyl ester membrane treated with 20% triethylamine in ethanol for 1 h.

2150 cm<sup>-1</sup> attributable to the diazoketone functionality and the development of a new band at ca. 1730 cm<sup>-1</sup> characteristic of an aliphatic ester.<sup>4</sup> It would appear that the transformation shown as the first reaction in Scheme 1 is occurring.

A detailed examination of the photochemically modified membranes was undertaken using SEM and other related techniques. Irradiation of the thin-film composite membrane in the presence of a 10% solution of 2-bromoethanol in diethylether causes a substantial change in the membrane surface structure. As can be seen in Figure 1(b), the original "honey-comb" surface structure of the diazoketone membrane<sup>4</sup> ([Fig. 1(a)] was found to be partially smoothed during the irradiation leaving void spaces in the coating. However, the overall thickness of the coating layer remained about 1500 nm.

Increasing the concentration of bromoethanol in diethylether to 20 and 30% (by volume) in the contacting diethylether solution, during the irradiation, resulted in the formation of surface coatings that were smooth and dense. The thicknesses of the films were measured and shown to be in the range of 500–1000 nm when 20% bromoethanol in ether was used in the photoreaction [Fig. 1(c)]. With the higher concentration of bromoethanol (30%) the film thickness was reduced to ca. 200 nm [Fig. 1(d)]. This reduction in thin-film thickness with increasing concentration of bromoethanol is clearly evident in Figure 1. The decrease in thin-film thickness is likely caused by a partial solubilization and collapse of the surface coating. This change is similar to, but more dramatic than, that noted previously with ethyl ester membranes.<sup>4</sup>

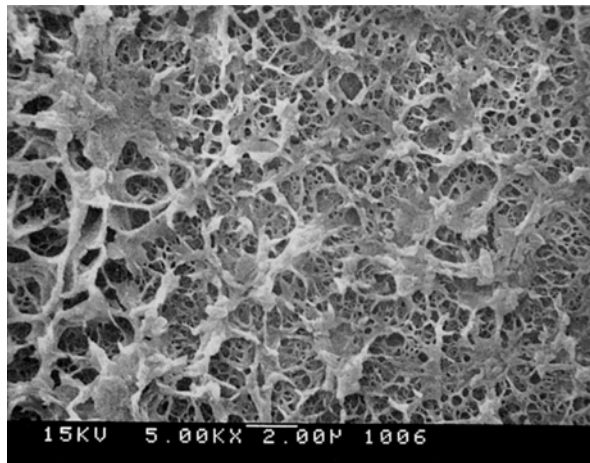
A SEM/EDS (energy dispersion spectrometer) cross-section line profile of Br for a membrane irradiated in 20% bromoethanol is presented in Figure 2. The micrograph presents, from right to left, part

of the fingerlike voids in the polysulfone (PS) support membrane, the structure near the surface of the PS support, and the thin-film coating (with part of the membrane surface visible). This line scan indicates clearly that Br is present in the surface layer. The Br signal rises sharply at the membrane surface. The trailing off of the signal through the PS membrane is most likely due to residual signal from the surface layer.

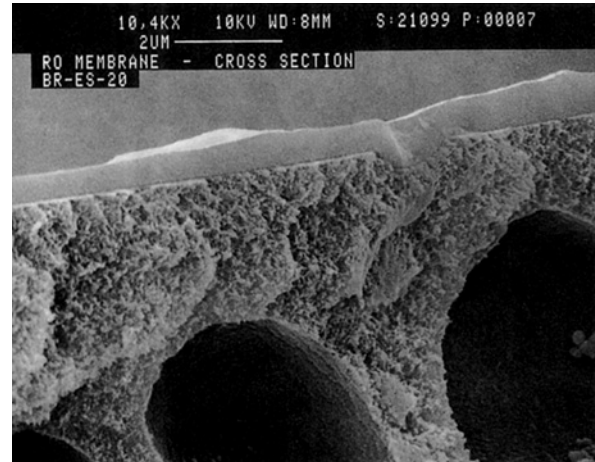
#### ESCA Analysis of Bromoethyl Ester Membranes

The surfaces of the bromoethyl ester membranes were examined using electron spectroscopy for chemical analysis (ESCA) to detect the presence of bromine (among other elements). The energies of the photoelectrons are specific to particular elements and the ionization states. This technique is able to analyze the outermost 3–10 nm on the membrane surface over sampling areas of about 1 mm in diameter with errors in the 0.1–0.5 atomic % concentration range. Data were collected from several locations on the membrane surface. The analyses were reproducible across the membrane surface suggesting a homogeneous polymer coating.

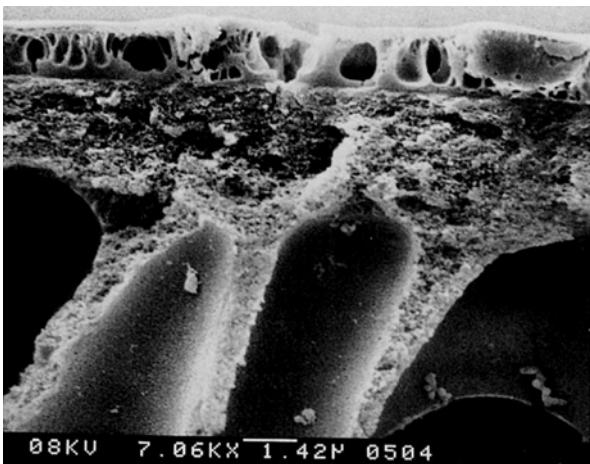
Conversion of all the diazoketone groups to bromoethyl ester, as in Scheme 1, should give a polymer with a repeat unit of (C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>N<sub>2</sub>S<sub>2</sub>Br)<sub>n</sub> (neglecting crosslinking). The elemental composition of such a polymer is given in Table II. The ESCA results presented in Table II (of bromoethyl ester membranes produced from 20% bromoethanol solution) confirm the presence of bromine in the thin film. However, the amount of bromine present is less than that expected from theory. Comparison of the two sets of data confirms the overall polymer structure but the actual amount of Br present is about one-third of that expected. Crosslinking at



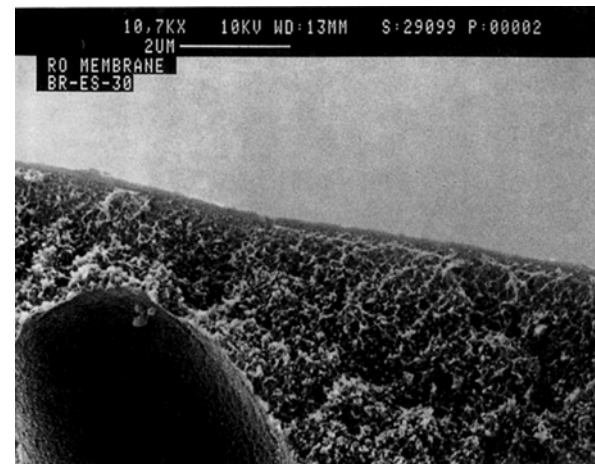
(a)



(c)



(b)



(d)

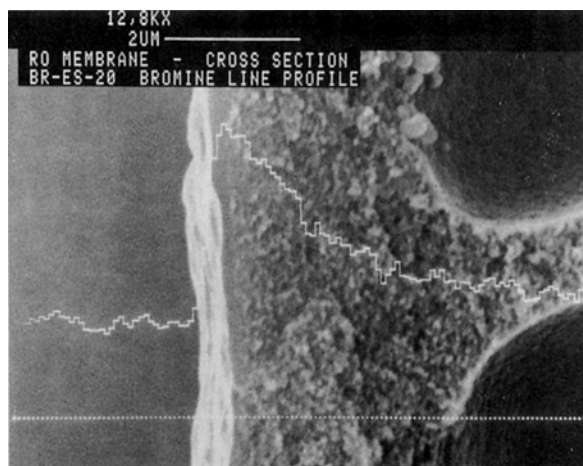
**Figure 1** SEMs of bromoethyl ester membranes produced from: (a) diazoketone membranes irradiated at 350 nm in (b) 10%, (c) 20%, and (d) 30% by vol 2-bromoethanol in diethylether solutions.

the 5% level used with these membranes cannot account for the difference between the measured and theoretical amount of Br. Apparently the bromoethanol is not being completely incorporated during the photochemical reaction, possibly due to the presence of traces of water in the contacting solution during the photochemical reaction, or that once the bromoethanol is bonded to the polymer some bromine is being lost due to a further thermal reaction.

The reverse osmosis properties of these photochemically modified membranes were examined using the four solutes listed in Table I. The effect of the photochemical modification and production of

the bromoethyl ester derivative was to reduce both the solution flux of the membrane by about 50% and the separation by an average of 10%.

Overall it is clear from these results that a photochemical modification of the membranes has indeed occurred to incorporate 2-bromoethanol as an ester grouping. While there is some question as to the degree of bromoethanol incorporation, the ATR-FTR results indicate that virtually all of the diazoketone is reacted and at least one-third of the diazoketone groups have been replaced by bromoethyl ester groups. Also, although the morphology of the thin film has changed during the irradiation, the



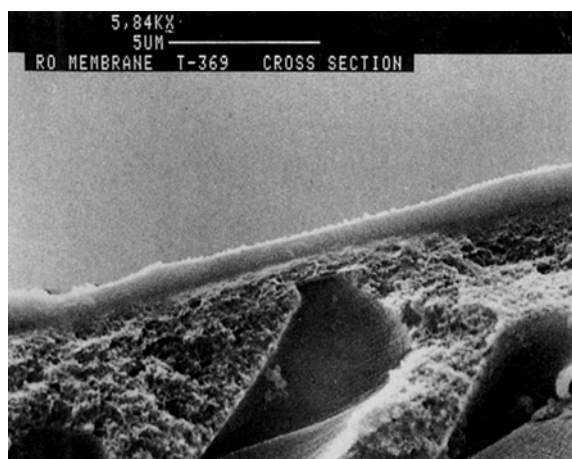
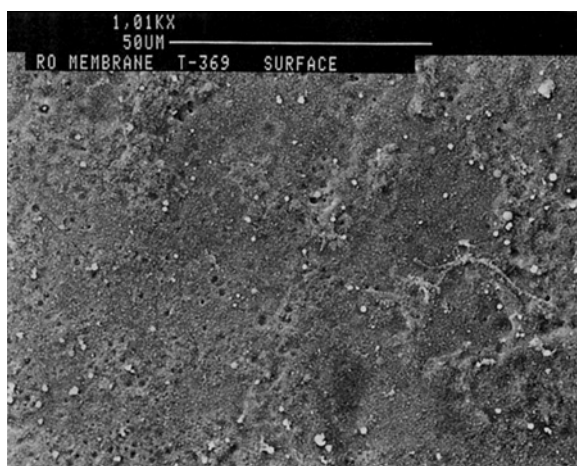
**Figure 2** SEM/EDS (cross section) Br line profile for a DK membrane irradiated at 350 nm in a 20% 2-bromoethanol in diethylether solution.

integrity of the membrane has been maintained and it continues to function as a reverse osmosis (RO) membrane.

#### Reaction of the Bromoethyl Ester Membranes with Triethylamine

Bromoethyl ester membranes (prepared from 20 vol % bromoethanol in diethylether) were treated with a 20 vol % solution of triethylamine in ethanol for 1 h in an attempt to replace the bromine atoms by an amine function, Scheme 1. The resulting membranes were examined by SEM (Fig. 3). From these micrographs the surface coating is a smooth, thin, dense layer of about 800 nm thickness; about the same as the original bromoethyl ester membrane.

The triethylamine-treated membranes were also examined by ESCA. The heavy atom elemental

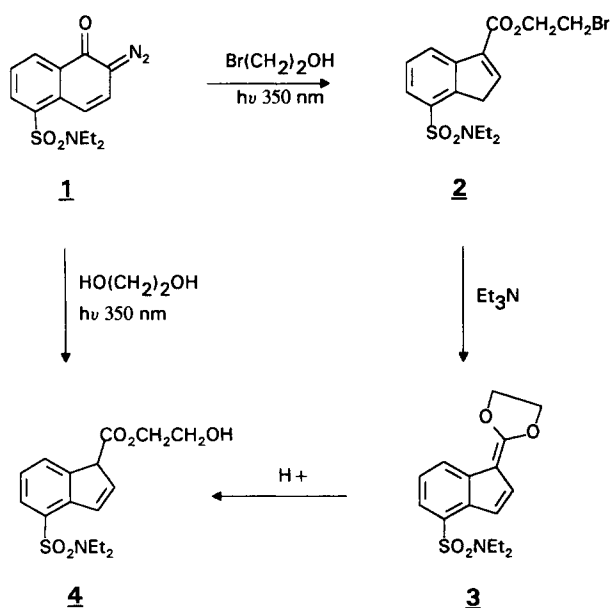


**Figure 3** SEM of a dioxolan membrane made from a 20% bromoethyl ester membrane treated with triethylamine: (a) surface view, and (b) edge on view.

**Table II** ESCA Elemental Composition for Bromoethyl Ester and Dioxolan Membrane Samples Compared to Theory

Measured	ATOMIC % CONCENTRATION				
	C	O	S	N	Br
BROMOESTER	64	20	7.3	7.2	1.1
DIOXOLAN	63	20	7.5	6.8	0.29
CALCULATED <sup>a</sup>					
BROMOESTER	62	21	6.8	6.8	3.4
DIOXOLAN	64	21	7.2	7.2	0

<sup>a</sup> Theoretical values of heavy atoms calculated on simple repeating polymer unit with no cross linking. Hydrogen atom content neglected in atomic concentration calculations.



analysis is given in Table II; there is a substantial reduction in the bromine content of the thin-film polymer. However, from the data in Table II, there was no increase in the proportion of nitrogen present as would have been expected if the desired nucleophilic displacement reaction proposed in Scheme 1 had taken place.

### Reactions with Model Compounds

In order to understand the reactions of these systems in more detail, the solution chemistry of a model diazoketone **1** was examined. The photoreaction of **1** with 2-bromoethanol occurred with the formation of the expected bromoester **2**, Scheme 2. The bromoester **2** was fully characterized spectroscopically. Treatment of **2** with a 20% solution of triethylamine in ethanol for 1 h yielded a new compound identified as the dioxolan **3**. Nuclear magnetic resonance (NMR) and mass spectral data of **3** were fully consistent with the assigned structure.

The dioxolan ring of **3** was shown to be labile and irreversibly opened on treatment with trifluo-

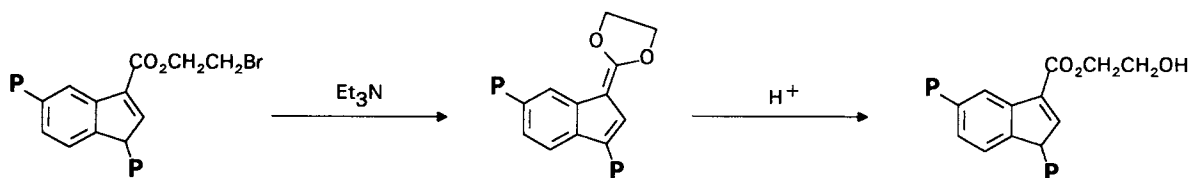
roacetic acid in water to give a new compound identified as **4**. Alternatively, **4** could also be produced directly from **1** by irradiation in the presence of ethylene glycol.

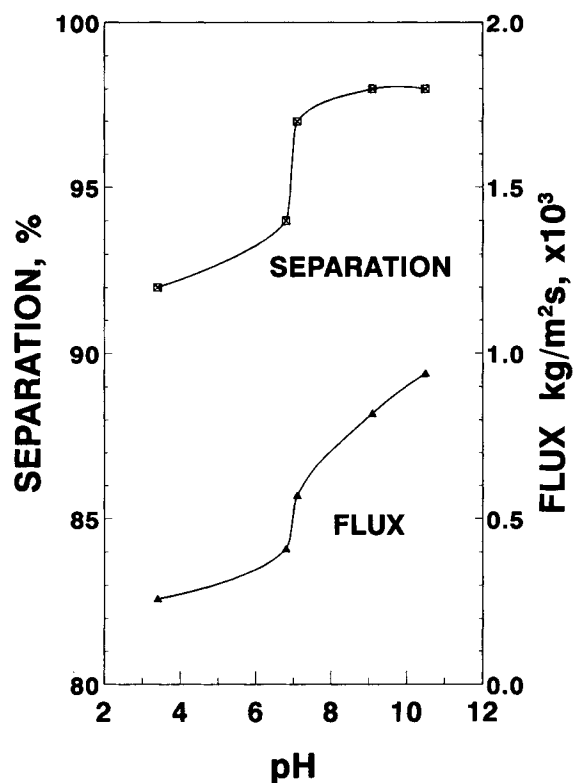
The conversion of **2** to **3** can be understood in terms of an ionization of the indenyl ring of **2** in the presence of triethylamine as a base followed by intramolecular displacement of bromine. Ring opening of **3** in acid would involve protonation of the fulvenyl bond to generate an intermediary dioxanylium ion.<sup>11</sup> In view of the facile nature of the ring closure of **2** to give **3** and subsequent ring opening in acid to give **4**, likely similar reactions are taking place with the bromoester membranes, Scheme 3.

### Reverse Osmosis Properties of the Chemically Modified Membranes

The flux and separation properties of the membranes obtained on treatment of a bromoethyl ester membrane with triethylamine are shown in Table I (DIOXOLAN). Compared to the bromoethyl ester membrane, the solution flux was typically lowered by more than an order of magnitude to less than  $0.4 \times 10^{-3} \text{ kg/m}^2 \text{ s}$ . However, the separation of NaCl was raised by a factor of over 3, to 88%. It should be noted that there was considerable variability between batches in the properties of these amine-treated membranes.

Exposing the dioxolan membranes to a dilute acid solution (NaCl/HCl pH 3) in the RO test system led to a further irreversible change in membrane performance. The NaCl-water separation rose to a 98% level (pH > 8) while the flux remained at about  $0.4 \times 10^{-3} \text{ kg/m}^2 \text{ s}$ . In the process of treating the membranes with acid, the separation for NaCl as a function of the pH of the feed solution was explored. From Figure 4 the effect of varying the pH of the NaCl feed solution was to produce titrationlike curves with both flux and separation increasing with increasing pH. The results were repeatable as the pH was cycled through different values from acidic to basic and back to acidic. These results indicate that the membrane became charged at higher pH leading to both higher flux and separation than at low pH.





**Figure 4** Reverse osmosis separation and solution flux of NaCl vs. pH for a hydroxyethyl ester membrane produced from a ring-opened dioxolan membrane.

The reproducibility of the performance changes with pH suggests that the acid treatment process converted the dioxolan groups to the hydroxyethyl ester functionality (Scheme 3) as found with the model compounds above.

In order to determine whether the pH dependence of these membranes is associated specifically with the 2-hydroxyethyl functionality or is a general property of ester-functionalized membranes of this type, the effect of the pH of the feed solution on separation/flux properties of a methyl ester membrane was examined. The methyl-ester-substituted membrane was produced as previously described by irradiation of the DK membrane in the presence of methanol.<sup>4</sup> Both of the ester-derivatized membranes exhibited similar pH dependency. In both cases there was a marked change, similar to that seen for ACID membranes in Part I,<sup>4</sup> in separation and flux at a pH value of approximately 7. The similarity between the two types of membrane suggests a common origin for this phenomenon.

Compound **5**, a good model for the polymeric indenyl system forming the thin-film layer was produced from the corresponding sulfonyl chloride (TCI

America) and diethylamine by the same method used to produce compound **1** and subsequent irradiation in methanol as previously described.<sup>2</sup> The  $pK_a$  value of the process shown in Scheme 4 was determined using ultraviolet (UV) measurements in several methanol-water buffer solutions<sup>12</sup> and calculated as approximately 6.5 using the following equation:

$$pK_a = \text{pH} - \log_{10} \left[ \frac{A}{\epsilon x - A} \right]$$

where

$A$  = absorbance of the indene ester anion at buffer pH

$\epsilon$  = molar extinction coefficient of indene ester anion in buffer

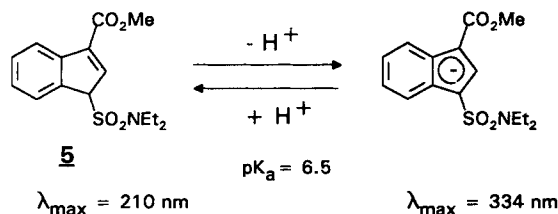
pH = pH of buffer solution

$x$  = total ester concentration.

The above evidence, for both model compounds and with membranes, supports that a hydroxyethyl ester moiety is being formed upon treatment of the bromoester membrane with triethylamine and an acid solution.

#### Direct Synthesis of Hydroxyethyl Ester Membranes

For comparison purposes, diazoketone membranes were directly converted to the hydroxyethyl ester form by irradiating the membrane at 350 nm in a solution consisting of 10% ethylene glycol in diethylether for 10 min. Typical RO results of these and control membranes are shown in Table III. After irradiation in alcohols, typical ester-functionalized membranes tend to exhibit lower solution fluxes, shown in our previous work.<sup>4</sup> This flux decrease was not observed in the case of the directly produced hydroxyethyl ester membranes. In fact, both the solution flux and solute separation are enhanced in these hydroxyethyl ester membranes as compared to the controls. This effect is likely due to the more



**Scheme 4**



**Table III Reverse Osmosis Performance Characteristics for Control and Hydroxyethyl Ester Membranes<sup>a</sup>**

Membrane	Solute (Flux Sep%)							
	NaCl		MgCl <sub>2</sub>		Na <sub>2</sub> SO <sub>4</sub>		MgSO <sub>4</sub>	
DIAZOKETONE	5.0	38	4.2	56	4.1	70	4.0	74
HOEtOH/Et <sub>2</sub> O SOAK <sup>b</sup>	6.4	38	5.5	64	5.3	74	5.3	83
HYDROXYESTER <sup>c</sup>	5.5	78	5.0	72	5.2	91	5.2	93

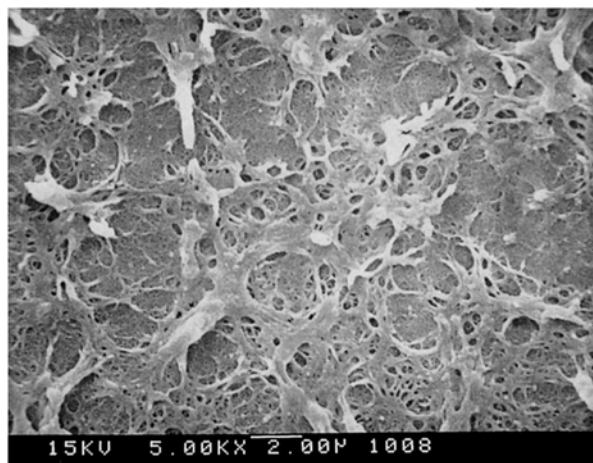
<sup>a</sup> Average of two or more membrane samples. Salts at 0.17M at pH approx 6. Tested at 6000 kPa with temperature at 25 ± 2°C. Fluxes corrected to 25°C. Flux in kg/m<sup>2</sup> s × 10<sup>3</sup>.

<sup>b</sup> Control DK membrane soaked in a 10% ethylene glycol in diethylether solution.

<sup>c</sup> Produced directly by irradiation of DK membrane in 10% ethylene glycol in diethylether.

hydrophilic nature of the hydroxyester than the ester on the membrane surface. The membranes produced by direct irradiation in ethylene glycol exhibited the same pH profile as those seen for the ring-opened (triethylamine-acid-treated) dioxolan and methyl ester membranes discussed previously supporting the assignment of this type of functionality to the acid-treated dioxolan membranes discussed above.

Unlike the photoreactions in the presence of 2-bromoethanol, SEM studies of the membranes produced by irradiation in the presence of diethylether solutions of ethylene glycol show no significant differences in surface morphology from the diazoketone precursor membranes (Fig. 5). Comparison of the RO results in Tables I and III suggests that the dramatic decrease in flux of the hydroxyethyl ester membranes formed from the ring-opened dioxolan



**Figure 5** SEM of a hydroxyethyl ester membrane produced directly from a diazoketone membrane irradiated at 350 nm in a 10 vol % solution of ethylene glycol in diethylether.

membranes must be due mainly to structural changes in the surface coating induced in the initial photochemical step. Likely, the dioxolan membrane solute separation is enhanced due to the more dense coating layer and the hydroxyethyl ester functionality while the decreased flux is primarily due to the dense coating. These results suggest that the photochemical derivatization process we have been developing for altering the surface functionality of a thin-film composite membrane can, with certain reagents, lead to an alteration in the physical structure of the thin film.

## CONCLUSIONS

This work presents a method for fabricating reverse osmosis membranes that can be modified by a photochemical technique. Conversion to bromoethyl ester functionality by irradiating in 2-bromoethanol and subsequent treatment with triethylamine resulted in drastic physical and chemical changes to the membrane. That a cyclization occurs upon treatment with triethylamine to an indene-dioxolan and a subsequent ring opening, in acidic media, to a hydroxyethyl ester has been confirmed on model compounds in solution. It is reasonable to expect that similar chemistry is taking place on the membrane surface. This physicochemical change resulted in excellent RO performance. The nascent diazoketone membrane (before photochemical reaction) had an open cellular surface structure. Photochemical conversions to bromoethyl ester and 2-hydroxyethyl ester membranes had thin dense surface layers suitable to RO applications. Surface analysis techniques of ATR-FTIR, SEM, SEM/EDS, and ESCA proved useful to monitor the physicochemical nature of the membranes.

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