Fabrication of Thin-Film Composite Membranes with Pendant, Photoreactive Diazoketone Functionality

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ABSTRACT: A disulfonyl chloride monomer having a pendent photoreactive diazoketone functional group has been synthesized in high overall yield ($>90\%$). The synthesis involves a convenient two-step reaction sequence starting from commercially available 6-diazo-5-oxo-5,6-dihydro-1-naphthalenesulfonyl chloride, which was reacted with piperazine then 1,3,6-naphthalenetrisulfonyl chloride to give the disulfonyl chloride diazoketone. Thin-film composite membranes having photoreactive diazoketone moieties as side chains of a polysulfonamide have been successfully fabricated by interfacial polymerization of ethanediamine with the disulfonyl chloride diazoketone on a polysulfone support. The effect of polymerization parameters such as monomer concentration, polymerization time, crosslinking, and surfactant have been systematically investigated in terms of membrane morphology and permeation properties. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2381–2398, 1997

INTRODUCTION

Optimization of the chemical nature and physical structure of a thin-film composite membrane can be a lengthy task.[1,2] Any change in the polymer selected for either the base membrane or the thin film requires that such an optimization be undertaken. In order to obviate this optimization step it is attractive to consider simple routes to modify the chemical nature of a membrane after it has been formed.[3,4]

A variety of methods have been used to modify the chemistry of membranes. These include conventional chemical modification,[5,6] plasma modification,[7-9] graft polymerization,[10-15] and photo-

chemical modification by direct irradiation of a membrane with short wavelength light.[16] Frequently, these methods have poor reproducibility and often lead to a relatively low degree of modification. Typically, high degrees of modification lead to a degradation of the initial membrane materials.

At McMaster we have been exploring the incorporation and use of photochemically active functional groups into the active layers of membranes.[4,17-19] In principle, this approach provides a flexible vehicle for the modification of the chemistry of the active layer. The incorporation of photochemically active groups can conveniently be accomplished by the use of derivatized monomers in an interfacial polymerization to form a thin-film composite (TFC) membrane. Diazoketone functionality was chosen as the photochemically active group for incorporation, as the photochemistry is reasonably well understood and this group can potentially be transformed selectively to a wide range of chemical functionalities (Scheme 1).[20-26] The diazoketone chromophore absorbs at long wavelengths, allowing selective photochemi-
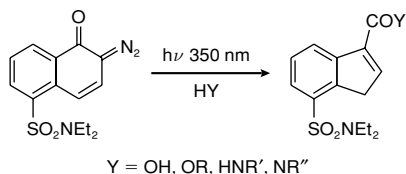
Scheme 1 Photochemical transformation of model diazoketone.

cal activation of the group without degradation of the polymer support. In this use of diazoketones in the polymer films we are seeking to retain the integrity of the film rather than solubilize it as in photoresist chemistry.[27-29]

Despite the obvious potential of this route for surface modification of TFC membranes, the existing delivery system needed to be improved. The monomer used in previous work was prepared by a difficult seven step synthesis in low overall yield. Moreover, the diazoketone functional group was incorporated into the backbone of the thin-film polymer and, as such, this could lead to a change in conformation of the polymer because the photochemical reaction converts a six-membered ring into a five-membered ring (Scheme 1).

In order to overcome these difficulties we have developed and describe here a new class of photochemically active TFC membranes in which the diazoketone functionality is incorporated into a side chain of a polysulfonamide backbone.

EXPERIMENTAL

Materials

6-Diazo-5-oxo-5,6-dihydro-naphthalenesulphonyl chloride was obtained from Fluka. 1,3,6-Naphthalene trisulfonyl trichloride (NTSC) was prepared from 1,3,6-naphthalene-trisulfonic acid trisodium salt and phosphorus pentachloride according to published methods.[19]

General Equipment

[1]H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AM500 and AC200 NMR spectrometers, respectively. The chemical shifts were measured relative to tetramethylsilane. UV spectra were recorded on a Hewlett Packard 8451A Diode Array spectrophotometer. Infrared spectra were obtained using a

Bio-Rad Digilab FTS-40 spectrometer. Mass spectra were recorded on VG ZAB-E Mass Spectrometer.

Chemical Syntheses

6-Diazo-5-oxo-5,6-dihydro-1-naphthalene piperazinesulfonamide, 3

Method 1: a solution of 6-diazo-5-oxo-5,6-dihydro-1-naphthalenesulfonyl chloride **1** (2.00 g, 7.4 mmol) in 50 mL of toluene was slowly added to a solution of piperazine **2** (1.28 g, 14.8 mmol) in 100 mL of toluene. The mixture was stirred at room temperature for 8 h. Piperazine hydrochloride was removed by gravity filtration and the filtrate was concentrated by evaporation of the solvent using a rotary evaporator until crystallization started. The solution was kept at ca. −13°C for 2 days. The product was collected by filtration, washed twice with ice-cold toluene, and dried *in vacuo* to give 1.93 g (82.3%) of a yellow needle-like crystalline product, **3,** m.p. (decomp.) 124–125°C. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 2.89 (t, J = 4.9 Hz, 4 H, CH$_2$), 3.12 (t, J = 4.9 Hz, 4 H, CH$_2$), 7.07 (d, J = 10.0 Hz, 1 H, H-8), 7.55 (t, J = 7.8 Hz, 1 H, H-3), 7.56 (d, J = 10.0 Hz, 1 H, H-7), 8.26 (dd, J = 7.7 Hz, J = 1.4 Hz, 1 H, H-4), 8.62 (d, J = 7.9 Hz, 1 H, H-2). ^{13}C-NMR (125 MHz, CDCl$_3$) δ 45.60, 46.48, 78.40 (C—N$_2$), 113.70, 118.85, 126.05, 131.04, 131.46, 133.38, 134.93, 135.20, 178.41 (C O). MS, m/z (rel. int.), 318 (M$^+$, 3), 290 (22), 142 (10), 113 (37), 85 (100). M$^+$ calc. for C$_{14}$H$_{14}$N$_4$O$_3$S 318.0787, found 318.0783. UV (CH$_2$Cl$_2$): λ_{max} = 398 nm, log ε = 3.80. IR (NaCl, cm^{-1}): 2162, 2115, 1621.

Method 2: the same procedure as outlined in Method 1 was followed except that dichloromethane was used as the solvent in place of toluene. In the final step the CH$_2$Cl$_2$ was removed *in vacuo* to give 2.29 g (96.6%) of a yellow powder **3.** The m.p., ^{1}H-NMR, and IR spectrum of the product prepared by Method 2 were identical to that obtained by Method 1.

1-[4-(2-Diazo-1-oxo-1,2-dihydro-5-sulfonyl)naphthalenyl-1-piperazinyl]sulfonyl-3,6-naphthalene disulfonyl chloride, 3-[4-(2-Diazo-1-oxo-1,2-dihydro-5-sulfonyl)naphthalenyl-1-piperazinyl]sulfonyl-1,6-naphthalene disulfonyl chloride, 6-[4-(2-Diazo-1-oxo-1,2-dihydro-5-sulfonyl)naphthalenyl-1-piperazinyl]sulfonyl-1,3-naphthalene disulfonyl chloride, 5

Method 1: a solution of the diazoketone amine **3** (0.10 g, 0.31 mmol) in 50 mL of dichloromethane

was added slowly to a solution of 1,3,6-naphtha-lenetrisulfonyl chloride **4** (0.14 g, 0.33 mmol) and pyridine (0.05 g, 0.63 mmol) in 100 mL of dichloromethane, and the resulting mixture stirred at room temperature for 8 h. After this time, the dichloromethane was evaporated at reduced pressure and the crude product examined by ^{1}H-NMR spectroscopy. The crude product was purified using silica gel column chromatography eluting with a mixed solvent containing toluene, diethyl ether, acetic acid, and methanol (120 : 60 : 18 : 1 v/v) to afford 0.10 g (45.5%) of the diazoketone **5** as a yellow powder. m.p. 164°C (decomp). ^{1}H-NMR (200 MHz, CDCl$_3$) δ 3.29 (s, 8 H, CH$_2$), 7.09 (d, $J = 10.0$ Hz, 1 H, H-8), 7.38 (d, $J = 10.0$ Hz, 1H, H-7), 7.55 (t, $J = 7.8$ Hz, 1H, H-3), 8.19 (d, $J = 7.8$ Hz, 1 H, H-4), 8.61 (d, $J = 7.8$ Hz, 1 H, H-2), 8.2–9.2 (m, multiple peaks of protons on naphthalene rings of the three isomers). ^{13}C-NMR (50 MHz, CDCl$_3$) δ 45.11, 45.56, 78.61 (C—N$_2$), 112.51, 119.87, 177.87 (C O), 126.18–144.68 (multiple peaks of the three isomers). UV (CH$_2$Cl$_2$) $\lambda_{max} = 396$ nm, log $\varepsilon = 3.66$. IR (NaCl, cm^{-1}) 2160.7, 2110.6, 1618.5. Elemental analysis calc. for C$_{24}$H$_{18}$N$_4$O$_9$S$_4$Cl$_2$: C, 40.85; H, 2.57. Found: C, 40.94; H, 2.72.

Method 2: a solution of the diazoketone amine **3** (5.6231 g, 17.66 mmol) in 50 mL of dichloromethane was added slowly to a solution of 1,3,6-naphthalene trisulfonyl chloride **4** (7.4822 g, 17.66 mmol) and pyridine (1.3970 g, 17.66 mmol) in 100 mL of dichloromethane. The mixture was stirred at room temperature for 8 h and then washed with (2 × 50 mL) 1% aqueous HCl solution, followed by 3 × 50 mL of water. The dichloromethane solution was dried over anhydrous Na$_2$SO$_4$, then evaporated at reduced pressure before drying *in vacuo* at 50°C overnight, to afford 11.86 g (95.2%) of the diazoketone **5** as a yellow powder. The ^{1}H-NMR, ^{13}C-NMR, UV, and IR results indicated that this product was the same as that obtained using method 1.

Solubility of 5 in Acetone : Carbon Tetrachloride (10 : 90 v/v)

CCl$_4$ was added, with stirring, to a solution of diazoketone **5** (1.0 g) in 25 mL acetone to make a volume of 250 mL. The suspension was stirred at 25°C for 3 h, before filtration by gravity. One hundred milliliters of the saturated solution was taken, and the solvents removed at reduced pressure and about 70°C to give a yellow solid. The

solid was dried *in vacuo* for 3 h and weighed. The solubility of **5** in acetone : carbon tetrachloride (10 : 90, v/v) was found to be 2.26 g/L. A similar procedure was used to determine the solubility of **5** in 20% (vol.) chloroform and 80% (vol.) carbon tetrachloride as 0.486 g/L.

Measurement of the Uptake of Ethanediamine by the Polysulfone Support Membrane

The polysulfone support membrane was soaked in chloroform : carbon tetrachloride (10 : 90, v/v) overnight and rinsed with ethanol and then water. The membrane was immersed in a 100 mL aqueous solution containing $5.89 \times 10^{-4}M$ of Triton X-114 surfactant and various amounts of 1,2-ethanediamine for 2.5 h and subsequently removed from the aqueous diamine solution and rolled with a plastic roller to remove the aqueous solution on the membrane surface. The membranes were titrated with 0.1 N HCl aqueous solution to give the uptake of 1,2-ethanediamine by the support polysulfone membrane. The concentration of 1,2-ethanediamine in the support membrane was calculated based on the total volume occupied by the membrane. Duplicate experiments were carried out, and the results averaged.

The uptake of 1,2-ethanediamine by the support polysulfone membrane from the aqueous solutions containing either no surfactant or 0.1 g/L of poly(ethyleneimine) and varying amounts of 1,2-ethanediamine was measured in a similar way to that described above.

Membrane Fabrication

The thin-film composite membranes were prepared by interfacial polymerization of the diazoketone **5** with ethanediamine **7.** The support polysulfone UF membrane (a machine cast proprietary membrane) was soaked in water overnight, then immersed in 100 mL of an aqueous 1,2-ethanediamine solution containing either Triton X-114 or poly(ethyleneimine) as a surfactant for 2.5 h. The concentration of ethanediamine was varied between $0.2M$ to $1.5M,$ Triton X-114 from zero to $1.06 \times 10^{-3}M,$ and poly(ethyleneimine) from zero to 7 g/L. The membrane was removed from the soaking solution, rolled with a plastic roller to remove any excess solution on the membrane surface, and immersed in 100 mL of a solution of the diazoketone **5** ($1.42 \times 10^{-3}M$) in ace-

tone : carbon tetrachloride (10 : 90, v/v) for a defined time period.

The thin-film composite membranes were prepared in the same way described above when using other solvent systems.

Measurement of the Membrane Morphology and Thickness

Morphologies and thicknesses of thin-film layers were measured by scanning electron microscopy (SEM). The membranes were fractured in liquid nitrogen. Specimens were mounted on a copper holder and coated with gold before observation. The cross-sections were observed at 80 kV and 20,000× magnification using a JEOL 1200 EX-II SEM.

Reverse Osmosis Experiments

The membranes were tested in a reverse osmosis (RO) radial flow test system, which consisted of a pump, six RO cells, a pressure gauge, and pressure regulator.[17] The feed solution was pressurized and circulated over the surface of the membranes at 6000 kPa for at least 4 days before any measurements were made.

The reverse osmosis experiments were carried out at 6000 kPa and 25 ± 2°C. The membrane area was 1.508×10^{-3} m^2, and the feed flow rate was 1.0 L/min. Samples of the permeate were collected at various time intervals to determine the permeate flux through the membrane (in kg/m^{2}s). The conductivity of the permeate and feed solution were measured (YSI Model 31) and compared with calibration curves to give solute concentrations in the permeate and feed solution, respectively.

The separation of solute was defined by:

$$\text{Separation},\% = (C_F - C_P)/C_F \times 100\%$$

where C_F and C_P are the solute concentration in the feed and permeate solutions, respectively. Duplicate membranes were tested under the same conditions and the results were averaged.

RESULTS AND DISCUSSION

Design and Synthesis of Monomer 5

The diazoketone **1** is commercially available. The key to its incorporation in a polymer as a cova-

lently bound pendant group was to react this sulfonyl chloride group with other molecules to produce a monomer with suitable difunctionality for use in an interfacial polymerization. As our previous work has involved the preparation of polysulfonamides, polymers that offer the promise of enhanced chemical stability over the more commonly used polyamides,[4,19] it was decided to prepare a monomer containing two sulfonyl chloride groups. This was accomplished as set out in Scheme 2.

The reaction of diazoketone **1** with **2** to give **3** was found to occur in high yield. The optimal conditions were with the use of a 1 : 2 molar ratio of **1** to **2** and a solvent in which the byproduct pyridinium hydrochloride **6** was insoluble and could be removed by filtration. With toluene as a solvent, **3** was obtained as a crystalline solid in 82% yield. The product was fully characterized and shown to have the indicated structure. Alternatively, **3** was prepared more conveniently with CH$_2$Cl$_2$ as the solvent. In this case, while the isolated material was not crystalline, the spectroscopic properties and melting point were identical to that of a sample prepared using toluene.
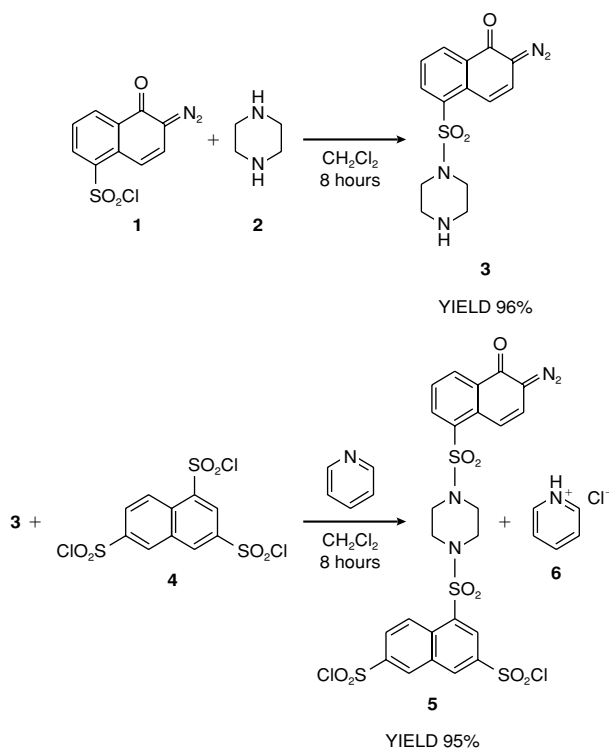
Scheme 2 Synthesis of the disulfonyl chlorides **5.**

The reaction of the amine **3** with the trisulfonyl chloride **4,** in CH$_2$Cl$_2$ with pyridine as a proton acceptor, yielded three isomeric products. Pyridinium hydrochloride and any excess pyridine was removed by washing with water. Examination of the product by NMR spectroscopy confirmed that **5** had been formed as a mixture of isomers. Attempts to isolate the disulfonyl chloride isomers using column chromatography were not successful and the mixture was used in the subsequent polymerizations. The mixture of isomers **5** was fully characterized using spectroscopic techniques and elemental analysis.
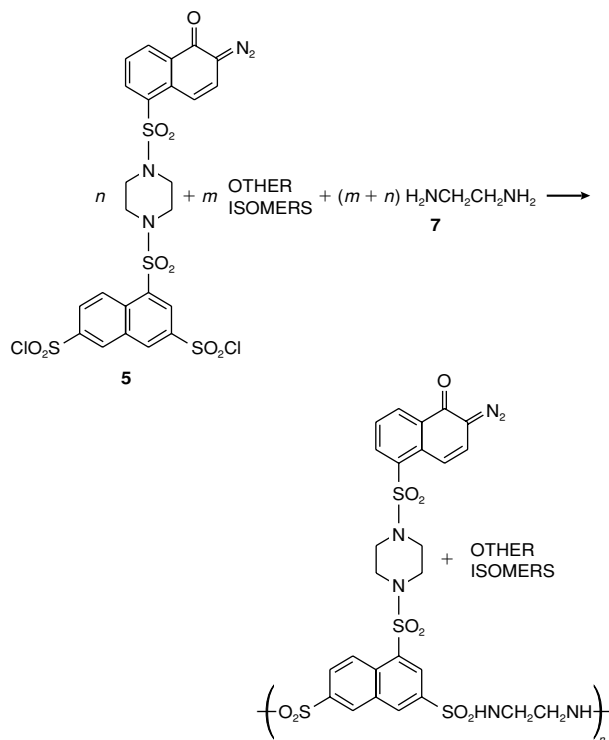
Solubility of the Disulfonyl Chlorides, 5

The interfacial polymerization step in the formation of a TFC is typically carried out with solutions of the diacid chloride in an organic solvent contacting an aqueous diamine solution contained within the pores of a support membrane. Leaving aside environmental considerations, the requirements for the selection of an organic solvent are stringent. The diacid chloride should be reasonably soluble in, but not react with, the organic solvent. The organic solvent must not dissolve or adversely affect the supporting base membrane (polysulfone). In addition, water and the organic solvent should be immiscible. Finally, the diamine should partition between the organic solvent and the aqueous phase.

The disulfonyl chlorides **5** are relatively large molecules and relatively insoluble in many organic solvents. While the disulfonyl chlorides **5** were essentially insoluble in CCl$_4$, a solvent commonly used in interfacial polymerizations, the addition of CHCl$_3$ or acetone to the CCl$_4$ improved the solubility. It has been reported that the supporting polysulfone ultrafiltration membrane is adversely affected by exposure to either CHCl$_3$ or acetone.[17] It was found in this work that the solvent mixtures CCl$_4$/CHCl$_3$ (80 : 20) and CCl$_4$/acetone (90 : 10) did not damage the supporting base membrane. These mixtures also exhibited reasonable solubilities of the disulfonyl chlorides **5,** namely, 0.486 and 2.26 g/L, respectively at 25°C.

Uptake of Diamine Monomer by the Support Polysulfone Membrane

Interaction of ethanediamine with the support polysulfone membrane was also examined. The

Scheme 3 Interfacial polymerization of the disulfonyl chlorides with 1,2-ethanediamine.

"uptake" of diamine by the support membrane was linearly related to the concentration of diamine in solution. Assuming that the polysulfone membrane occupies no space, a pseudo-partition coefficient K was determined as a relative measure of diamine partitioning. For aqueous ethanediamine solutions with no added surfactant, K was found to be 0.31. The addition of Triton X-114 surfactant (5.89×10^{-4} M) to the aqueous solution increased K to 0.48. In other words, there is an increase of ca. 50% in the amount of ethanediamine absorbed by the membrane when Triton X-114 is present. The origin of this effect is not completely clear; however, the substantial increase in diamine uptake by the polysulfone base membrane is associated with the presence of the surfactant.

Poly(ethyleneimine) did not act in the same manner as Triton X-114; no increase in K was observed on addition to the aqueous solution.

Interfacial Polymerization and Formation of TFC Membranes

The interfacial polymerization of the disulfonyl chlorides **5** with ethanediamine **7** (Scheme 3) was

Table I   Fabrication Conditions and Membrane Performance of Thin-Film Composite Diazoketone Membranes by Interfacial Polymerization of the Diazoketone 5 with a Diamine

| Membranes | Aqueous Phase | | | | Organic Phase | | Rxn Time h | Membrane Performance[b] | |
| | Surfactant | | 1,2-Ethanediamine M | Ethanol/Water v/v | Disulfonyl Chloride $\times 10^4 M$ | Type[a] | | FLUX $\times 10^3$ kg/m^{2}s | Separation (NaCl) % |
	Triton X-114 $\times 10^4$, M	PEI g/L							
A. Effect of Polymerization Time on Membrane Structure and Performance									
I-DK-T-01	5.9	—	0.67	0/100	6.9	I	0.25	20.8	23.9
I-DK-T-02	5.9	—	0.67	0/100	6.9	I	0.50	16.6	26.0
I-DK-T-03	5.9	—	0.67	0/100	6.9	I	1.0	13.6	24.0
I-DK-T-04	5.9	—	0.67	0/100	6.9	I	2.0	11.6	26.8
I-DK-T-05	5.9	—	0.67	0/100	6.9	I	3.0	11.8	23.9
I-DK-T-06	5.9	—	0.67	0/100	6.9	I	5.0	12.9	25.1
I-DK-T-07	5.9	—	0.67	0/100	6.9	I	10.0	14.1	22.1
I-DK-T-08	5.9	—	0.67	0/100	6.9	I	15.0	13.7	22.2
II-DK-T-01	5.9	—	0.67	0/100	14.2	II	0.25	9.7	29.8
II-DK-T-02	5.9	—	0.67	0/100	14.2	II	0.50	8.6	31.4
II-DK-T-03	5.9	—	0.67	0/100	14.2	II	1.0	7.5	31.4
II-DK-T-04	5.9	—	0.67	0/100	14.2	II	2.0	7.2	32.4
II-DK-T-05	5.9	—	0.67	0/100	14.2	II	5.0	6.8	33.9
II-DK-T-06	5.9	—	0.67	0/100	14.2	II	24	5.9	38.6
B. Effect of Triton X-114 Surfactant Concentration on Membrane Structure and Performance									
II-DK-0-00	0	—	0.67	0/100	14.2	II	2.0	21.9	17.8
II-DK-T-07	0.9	—	0.67	0/100	14.2	II	2.0	8.3	41.4
II-DK-T-08	5.9	—	0.67	0/100	14.2	II	2.0	10.9	37.2
II-DK-T-09	17.7	—	0.67	0/100	14.2	II	2.0	10.2	28.9

C. Effect of Ethanediamine Concentration on Membrane Structure and Performance

II-DK-PEI-01	—	0.1	0.17	0/100	14.2	II	2.0	46.9	22.2
II-DK-PEI-02	—	0.1	0.33	0/100	14.2	II	2.0	45.5	36.1
II-DK-PEI-03	—	0.1	0.50	0/100	14.2	II	2.0	44.2	47.1
II-DK-PEI-04	—	0.1	0.67	0/100	14.2	II	2.0	42.5	59.0
II-DK-PEI-05	—	0.1	0.9	0/100	14.2	II	2.0	39.7	55.5
II-DK-PEI-06	—	0.1	1.16	0/100	14.2	II	2.0	31.1	53.2
II-DK-PEI-07	—	0.1	1.41	0/100	14.2	II	2.0	23.7	55.5
II-DK-PEI-08	—	0.1	1.7	0/100	14.2	II	2.0	25.7	55.5

D. Effect of Poly(ethyleneimine) Concentration on Membrane Structure and Performance

II-DK-0-00	—	0	0.67	0/100	14.2	II	2.0	21.9	17.8
II-DK-PEI-09	—	0.03	0.67	0/100	14.2	II	2.0	32.6	53.6
II-DK-PEI-04	—	0.1	0.67	0/100	14.2	II	2.0	35.2	55.1
II-DK-PEI-10	—	7	—	0/100	14.2	II	2.0	16.6	56.6

E. Effect of Ethanol Volume Fraction in Aqueous Phase on Membrane Structure and Performance

II-DK-T-E-00	5.9	—	0.67	0/100	14.2	II	2.0	14.3	20.0
II-DK-T-E-01	5.9	—	0.67	25/75	14.2	II	2.0	—	—
II-DK-T-E-02	5.9	—	0.67	50/50	14.2	II	2.0	—	—
II-DK-T-E-03	5.9	—	0.67	75/25	14.2	II	2.0	27.9	30.7
II-DK-T-E-04	5.9	—	0.67	100/0	14.2	II	2.0	50.8	13.9

[a] Organic phase: I. volume ratio: $CCl_4/CHCl_3$ (80:20); II. volume ratio: CCl_4/aetone (90:10).
[b] Test conditions: pressure 6000 kPa, temperature $25 \pm 2°C$, feed solution: 0.17 M NaCl in water, 1.0 L/min. Results are the average of two or more membrane samples.
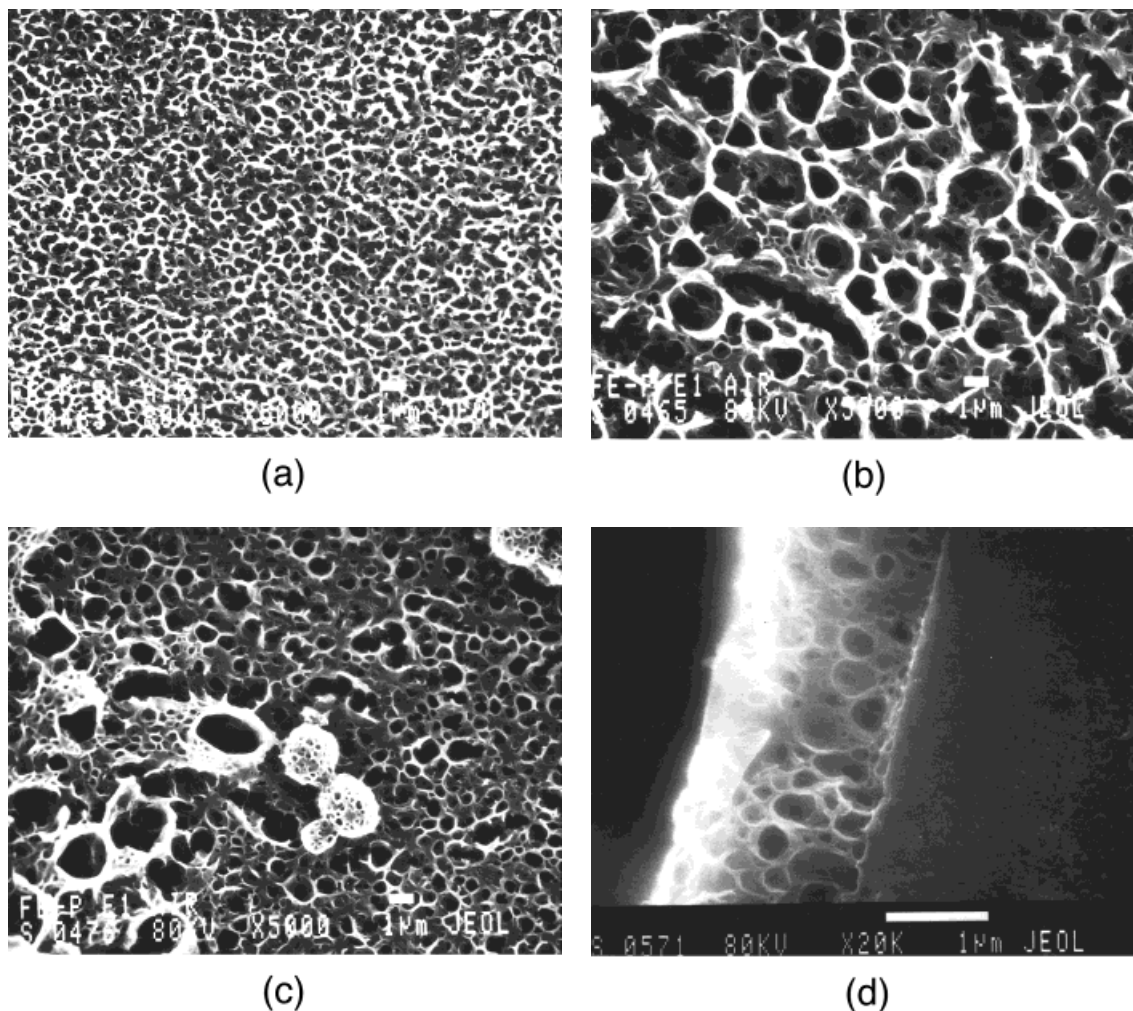
Figure 1   SEM photographs of the thin-film composite diazoketone membranes prepared using a $CCl_4/CHCl_3$ (80 : 20, v/v) solvent system. See Table 1A for details. Polymerization time and membrane No.: (a) 0.50 h, I-DK-T-02, (b) 1.0 h, I-DK-T-03, (c) and (d) 3.0 h, I-DK-T-05. (a), (b) and (c) top views, (d) cross-section view.

examined to determine the best conditions for producing a TFC membrane in terms of the permeability and morphology of the thin film. Because sulfonyl chlorides are substantially less reactive towards amines than carbonyl chlorides,[30-35] the reaction times for thin-film polymerization are much longer than those normally encountered in the preparation of polyamides. Despite this drawback, polysulfonamides have been prepared by interfacial polymerization routes.[19,36,37] The conditions used to prepare membranes in this work are summarized in Table I.

Use of the $CCl_4/CHCl_3$-H_2O System

The interfacial polymerization of the disulfonyl chlorides **5** in $CCl_4/CHCl_3$ (80 : 20, v/v) with

aqueous ethanediamine was examined. A polysulfone base membrane and the surfactant Triton X-114 were used. Examination of the resulting membranes (I-DK-T-01 to 08 Table I, part A) by scanning electron microscopy (SEM) showed that in each case polysulfonamide films were formed on the surface of the supporting polysulfone membrane. However, as can be seen in Figure 1, these films, particularly those produced using longer reaction times, had relatively open or porous morphologies. The thicknesses of the porous films (determined using SEM) were found to increase with increasing polymerization time (as illustrated in Fig. 2) up to approximately 3 h. After this time a limiting thickness of approximately 2 μm was reached.
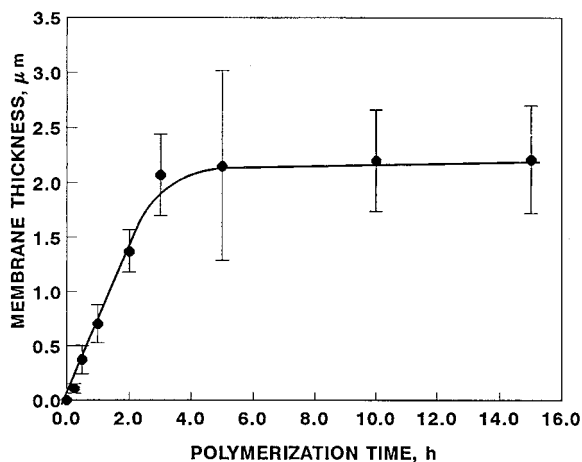
Figure 2 Effect of polymerization time on thickness of the thin-film composite diazoketone membranes with $CCl_4/CHCl_3$ solvent system. See Table I for details: I-DK-T-01 to I-DK-T-08.

The permeability of these membranes (Table I, part A) was examined using a $0.17M$ aqueous NaCl solution. All of the membranes exhibited a similar, relatively low separation (about 25%) for NaCl (Fig. 3). Because there was virtually no change in NaCl separation as the film thickness increased it was concluded that the separation of NaCl is determined primarily by a dense layer of sulfonamide polymer formed in the initial stages of the polymerization rather than by the thicker, more porous layer formed later in the polymerization. However, the increase in film thickness did have an effect on permeate flux (Fig. 3). A rapid drop in flux to 65% of the initial value was observed in membranes prepared with polymerization times approaching 1 h; membranes prepared with longer polymerization times had essentially constant flux. The leveling off of flux occurs after about 1 h polymerization time, whereas the maximum film thickness is reached only after 3 h. Presumably the open structured polymer added after 1 h of polymerization resulted in no additional resistance to permeation.

It was clear from these preliminary results that TFC membranes produced using the $CCl_4/CHCl_3$ organic solvent system were far from optimal in terms of their performance. The use of very short polymerization times led to poor reproducibility in membrane performance due to uneven coating of the polysulfone support. For these reasons other solvent systems in which the monomer **5** had a greater solubility were examined.

Use of CCl_4/Acetone–H_2O System

The solubility of the disulfonyl chlorides **5** in the CCl_4/acetone (90 : 10, v/v) solvent system is about 4.5 times larger than that in $CCl_4/CHCl_3$ (80 : 20, v/v). The use of acetone and related water-soluble solvents in the organic phase of an interfacial polymerization has been reported.[31] Water-miscible organic phase cosolvents appear to facilitate partitioning of the diamine into the organic phase thus accelerating the rate of polymerization.

Interfacial polymerizations of the disulfonyl chlorides **5** in the CCl_4/acetone (90 : 10, v/v) was examined at conditions summarized in Table I. SEM examination of membranes II-DK-T-01 to 04 showed that at longer polymerization times the film once more had a textured morphology; presented at two polymerization times in Figure 4. The pores appeared to have opened or burst to form an open texture throughout the thickness of the coating layer.

Examination of the permeation properties of the membranes (Fig. 5) produced using CCl_4/acetone as the organic solvent showed that the separation of NaCl was slightly improved while the flux was decreased by about 50%, compared to those formed with $CCl_4/CHCl_3$. The measured properties of the membranes had a similar drop in flux but slight increase in separation with in-

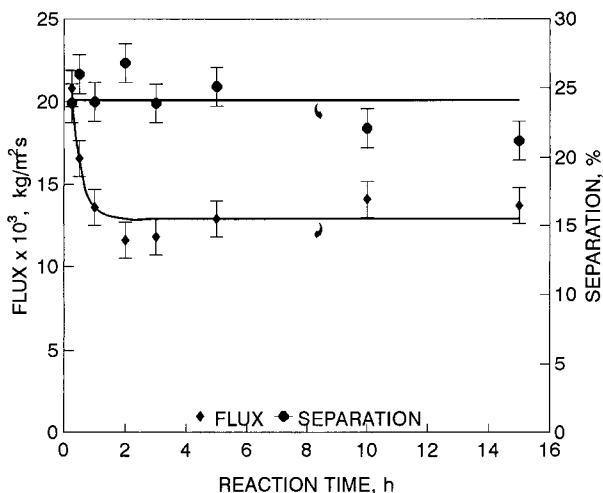**Figure 3** Effect of polymerization time on the performance of thin-film composite diazoketone membranes with $CCl_4/CHCl_3$ solvent system. See Table I for details: I-DK-T-01 to I-DK-T-08. Test conditions: pressure, 6000 kPa; temperature 25°C; feed, $0.17M$ NaCl aqueous solutions.
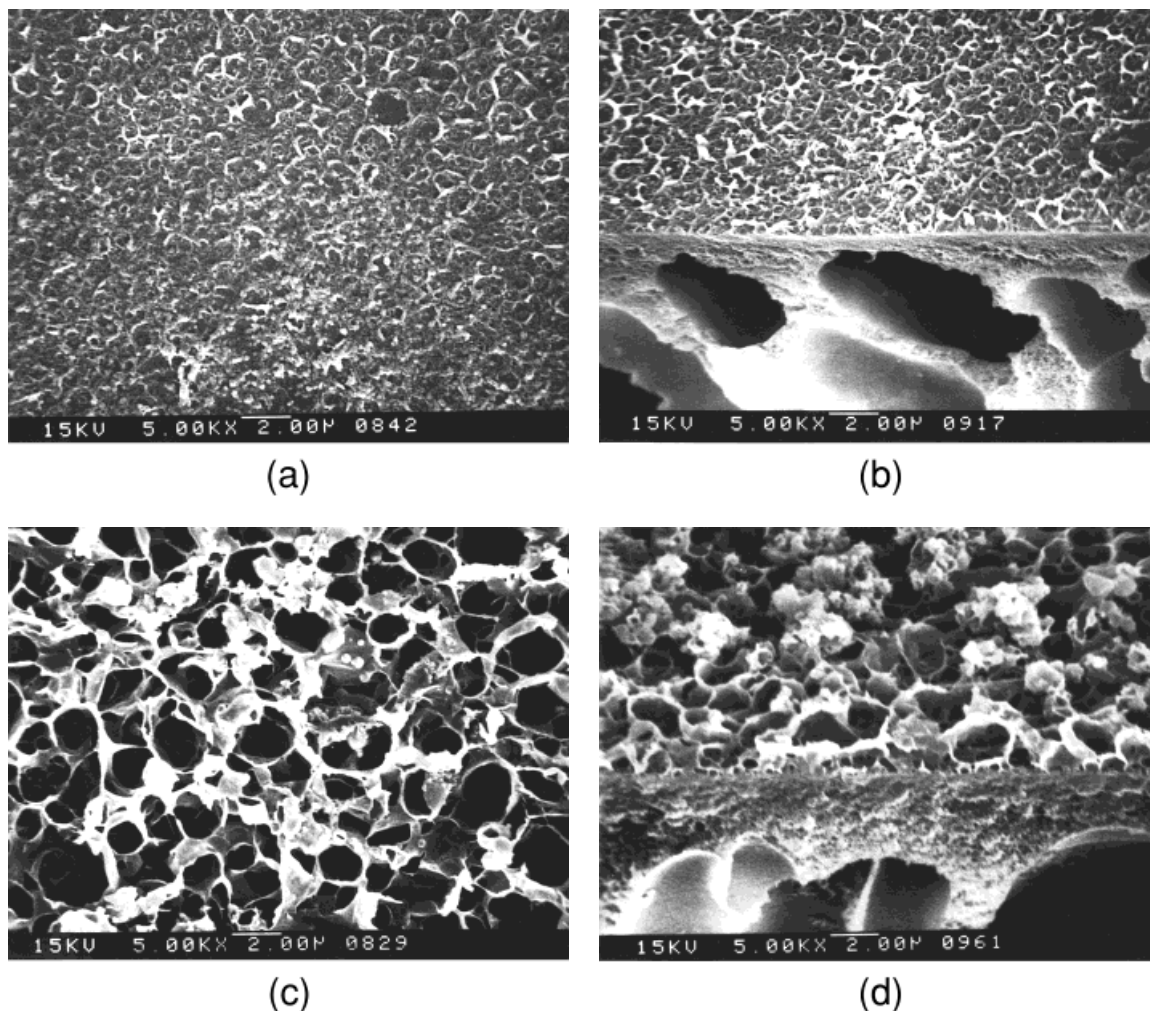
Figure 4 Effect of polymerization time on morphologies of the thin-film composite diazoketone membranes prepared using a CCl$_4$/acetone solvent system. See Table IA for details. Polymerization time and membrane No.: (a) and (b) 0.5 h, II-DK-T-02; (c) and (d) 2.0 h, II-DK-T-04. (a) and (c) top views, (b) and (d) edge-on cross-section views.

crease in polymerization time as compared to CCl$_4$/CHCl$_3$ as solvent. Again, considerable variability was found in membranes formed with the shortest polymerization times. Overall, it was clear from these results that an increase in the solubility of **5** in the organic phase of these interfacial polymerizations has a small effect on their performance but a fairly substantial effect on the coating morphology.

The concentration of surfactant (Triton X-114) used in the interfacial polymerization affected both the nature of the film formed and the permeability of the membrane. The open pore-type morphology was largely eliminated when the poly-

merization was carried out in the absence of any surfactant (Fig. 6). However, membranes formed without surfactant demonstrated a much reduced NaCl separation and increased permeate flux (Table I) membrane II-DK-0−00.

The use of poly(ethyleneimine)(PEI) as a surfactant was examined. The PEI can function as both a surfactant and a reactant in the interfacial polymerization.[38] The effect of PEI concentration on film morphology and permeability was examined using a standard polymerization time of 2 h. At the highest PEI concentration no ethanediamine **7** was present in the aqueous phase. TFC membranes were produced under all conditions.
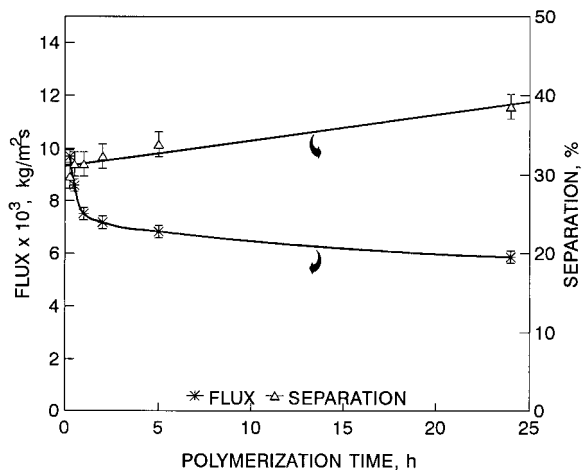
Figure 5 Effect of polymerization time on the performance of thin-film composite diazoketone membranes with CCl_4/acetone solvent system. See Table I for details: II-DK-T-01 to II-DK-T-06. Test conditions: pressure, 6000 kPa; temperature 25°C; feed, $0.17M$ NaCl aqueous solutions.

Even with these long polymerization times, relatively dense films were produced that seemed to lack the large pore type structures that were observed when Triton X-114 was used as the surfactant, as illustrated by SEMs in Figure 7. The membranes produced with PEI as a surfactant/ reactant displayed enhanced separations for NaCl (Table I, parts C and D). There was a large increase in flux for the membranes formed from ethanediamine and PEI as compared to those prepared without the addition of PEI. For example, comparing II-DK-0−00 and II-DK-PEI-09 (Table I, part D), the flux increased by about 50% and the separation approximately tripled upon addition of PEI.

The importance of the ethanediamine : PEI ratio was explored by systematically varying the concentration of ethanediamine while keeping that of PEI constant. The results of this study are shown in Figure 8. The separation of NaCl first increased and then reached a plateau at an ethanediamine concentration of $0.67M$. The measured fluxes decreased steadily as the ethanediamine concentration increased.

Speculation on the Mechanism of Thin-Film Formation

While the exact mechanism of membrane formation, and the role of the surfactant on this forma-

tion, is not known, the following speculation is reasonable. The surface of the membranes formed without surfactant, as illustrated in Figures 1 and 4, have open porous structures on the surface of the membranes, as discussed above. It would be reasonable to assume that these structures were formed as a result of penetration of the aqueous phase into the forming polymer film. The aqueous diamine solution can penetrate the slowly forming thin-film, form droplets and be surrounded by the organic solvent with disulfonylchloride. Polymerization would continue at the droplet surface forming closed cells of aqueous diamine surrounded by sulfonamide polymer; a similar mechanism for void formation during encapsulation by interfacial polymerization has been proposed.[39] In the final stages of the polymerization these cells can burst open as the surrounding polymer contracts, forming the open celled structure observed. Careful examination of Figures 1 and 4 reveal that within the cross-section of the thin film some closed cells still remain, apparently trapped in the thin film.

In the presence of Triton X-114 surfactant, a similar mechanism as above can take place. However, the surfactant affects the surface energy and size of the aqueous droplet such that the cells are more rigid and with the contraction of the polymer small holes burst in the surface leaving relatively intact cells (see Fig. 6). With the polyamine surfactant PEI (Fig. 7), the cells are closed and surrounded by bulk polymer giving a much more uniform coating.

The above hypothesis suggests that the structure of the surface coating can be influenced by other factors, such as the addition of a crosslinking agent or the cosolvent ethanol, which are examined below. Because the reaction times for these membranes are long and the separation is relatively low, typical of nanofiltration membranes, it would be difficult to commercialize these membranes. The reaction times and separation are probably related to the slow reaction rate of sulfonamide formation compared to rapid reaction rates in polyamide membranes.

Crosslinked Polysulfonamide Coatings

The effect of crosslinking on the membrane performance was examined by producing membranes with the addition of 5% by weight of NTSC **4** in the organic polymerization phase. The weight to volume ratio of sulfonyl chlorides to CCl_4/acetone
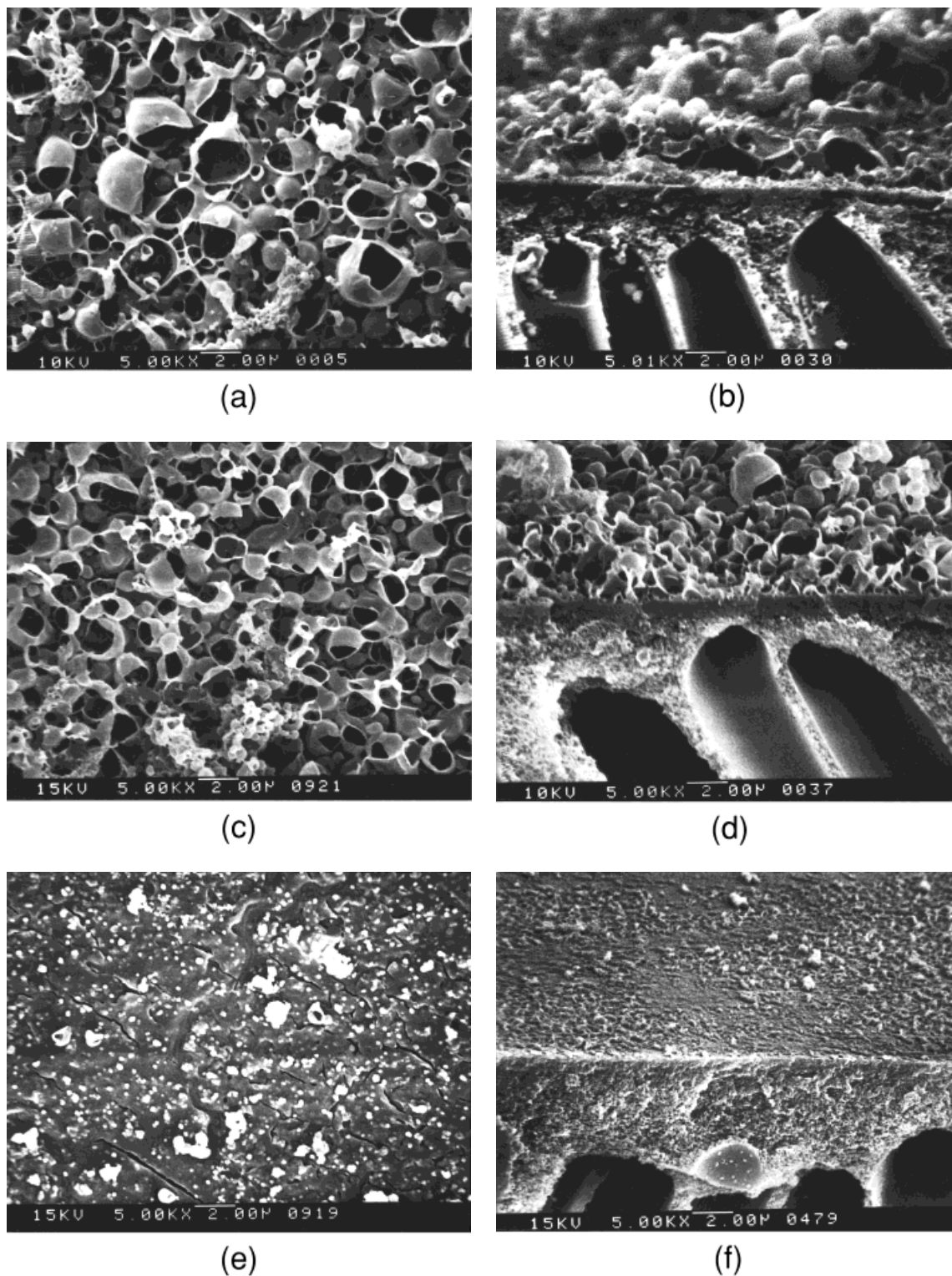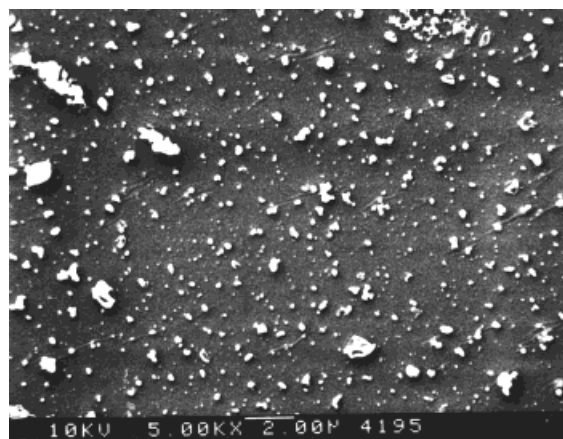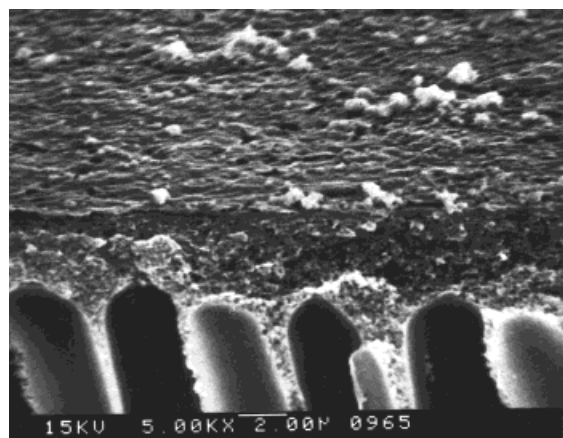
Figure 6 Effect of Triton X-114 surfactant in aqueous solution on morphologies of the thin-film composite diazoketone membranes. See Table IB for details. Concentration of Triton X-114 surfactant and membrane No.: (a) and (b) $17.7 \times 10^{-4} M$, II-DK-T-09; (c) and (d) $5.9 \times 10^{-4} M$, II-DK-T-08; (e) and (f) $0.0 M$, II-DK-0−00. (a), (c), and (e) top views, (b), (d), and (f) edge-on cross-section views.

(a)

(b)

Figure 7 Effect of poly(ethyleneimine) on membrane morphology. See Table IC for details. Membrane No.: I-DK-PEI-04, (a) top view, and (b) edge-on cross-section view.

was kept to 0.10. Two sets of crosslinked membranes were produced using polymerization times of 1 and 2 h. All other fabrication parameters were kept constant.

The reverse osmosis performance characteristics for these crosslinked membranes (designated by code prefix "X") are shown and compared to noncrosslinked counterpart membranes II-DK-T-03 and -04 in Table II. The results indicate that the addition of the crosslinking agent has a small but detrimental effect on membrane separation while increasing the solution flux by a factor of almost 3 for membranes produced with a 1 h polymerization time. At a 2 h polymerization time the addition of the NTSC has a negligible effect on

the membrane performance. This is likely because the film thickness and density has reached a maximum at 2 h.

At a 1 h polymerization time the crosslinking effects are significant. During the polymerization crosslinks are formed between polymer chains through the trifunctional NTSC and, as well, pendant sulfonic acid groups are produced from noncrosslinked sulfonyl chlorides. These pendant sulfonic acid groups make the membranes more hydrophillic, which may explain the increase in solution flux compared to the noncrosslinked membranes.

To further characterize these membranes, the pH of the NaCl test solution was varied by the addition of various amounts of HCl or NaOH and the reverse osmosis performance measured. As the pH of the feed solution was cycled from acidic to basic and back in the range from 3 to 10, there was little change in the flux or separation properties of all the membranes. This would indicate that the membranes produced are hydrolytically stable and, because there were no jumps in separation or flux, that the membrane surface is neutral in character.

In summary, the use of CCl_4/acetone as the organic solvent in interfacial polymerizations gave membranes with improved separations but decreased fluxes compared to those formed with
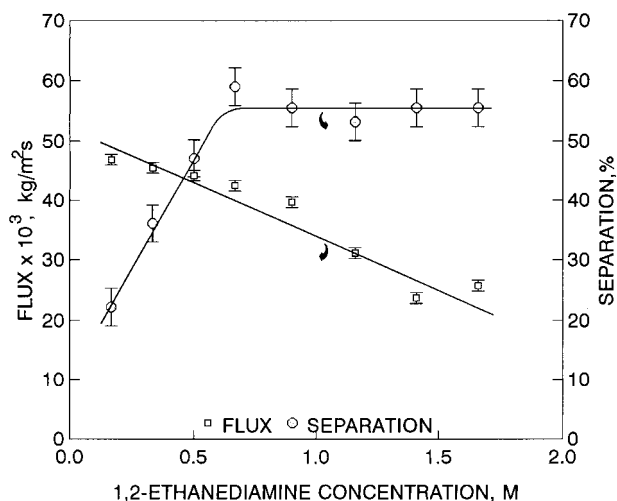

Figure 8 Effect of 1,2-ethanediamine monomer concentration in aqueous phase on the performance of thin-film composite diazoketone membranes with the CCl_4/acetone solvent system. See Table I for details. II-DK-PEI-01 to II-DK-PEI-08. Test conditions: pressure, 6000 kPa; temperature 25°C; feed, 0.17M NaCl aqueous solutions.

Table II   Reverse Osmosis Performance Characteristics of Crosslinked and Noncrosslinked Diazoketone Membranes[a]

Membrane	Polymerization Time, h	Flux $\times 10^3$, kg/m^{2}s	NaCl–H$_2$O Separation, %
II-DK-T-03	1	7.5	31
X-II-DK-T-03	1	20.2	25
II-DK-T-04	2	7.2	32
X-II-DK-T-04	2	11.8	34

[a] Test conditions as in Table I. Results are the average of two or more membrane samples.

CCl_4/$CHCl_3$. The morphology of the membranes produced with CCl_4/acetone was also different with a more open but still heavily textured surface with Triton X-114 as a surfactant. The membranes produced with PEI as a surfactant look promising; however, for the photochemical transformations intended with these membranes the unreacted amine functionality, present as a result of the use of PEI, could represent a limitation.

The improvement in the properties of the TFC membranes with addition of a water-soluble cosolvent to the organic phase suggested that it would be instructive to add an organic cosolvent to the aqueous phase. The use of water-soluble cosolvents such as ethanol in interfacial polymerizations has previously been reported.[31]

Use of a CCl_4/Acetone–H$_2$O/Ethanol System

Interfacial polymerizations of **5** were carried out using a standard 2-h reaction time, and concentrations of Triton X-114 ($5.9 \times 10^{-4}M$) and ethanediamine ($0.67M$). The volume ratio of ethanol to water was varied from 0/100 to 100/0. The results of this study are summarized in Figure 9 and Table I.

Examination of the morphology of the TFC membranes produced using these solvent systems indicated that relatively dense, nontextured thin films were formed when either pure ethanol or ethanol/water (75 : 25) was used as the solvent [Fig. 9(e–h)]. On the other hand, when the ratio of ethanol to water was 50 : 50 or less, there were variations in the nature of the open-textured surface; once more, rough surfaces were produced. Control experiments were performed in which a membrane formed without ethanol being present was subsequently soaked in ethanol for 24 h showed that the thin films were not significantly modified by the presence of ethanol. This result

means that the presence of ethanol in the "aqueous" phase affects the actual polymerization process and formation of the thin film. By the mechanism, speculated on above, the higher concentrations of ethanol are affecting the nature of the phase inversion and the subsequent membrane structure.

The separation and flux of these membranes was examined using NaCl solutions. There were increases in both flux and separation when an ethanol/water ratio of 75 : 25 was used in the interfacial polymerization step as compared to the control membrane having no ethanol present (Table I). This change is accompanied by the elimination of the open textured morphology of the membrane in the mixed solvent. However, there was a major increase in flux and a drop in separation with membranes produced using just ethanol as a solvent for the ethanediamine.

Characterization of TFC Membranes

The nature of the membranes produced from the interfacial polymerization of the diazoketone **5** and ethanediamine was examined in two ways. First, the surface functionality was probed using reflectance IR spectroscopy and, second, the permeability of the membranes to a series of salts was studied in order to gain information on any charge present in the barrier layer.

The attenuated total reflectance FT–IR spectra of the base polysulfone membrane and a TFC membrane are presented in Figure 10. The key additional feature in the TFC membrane is the presence of two strong absorptions just above 2000 cm^{-1} that are characteristic of the diazoketone functionality. It is clear that the interfacial polymerization has led to the incorporation of the desired photochemically active diazoketone group.
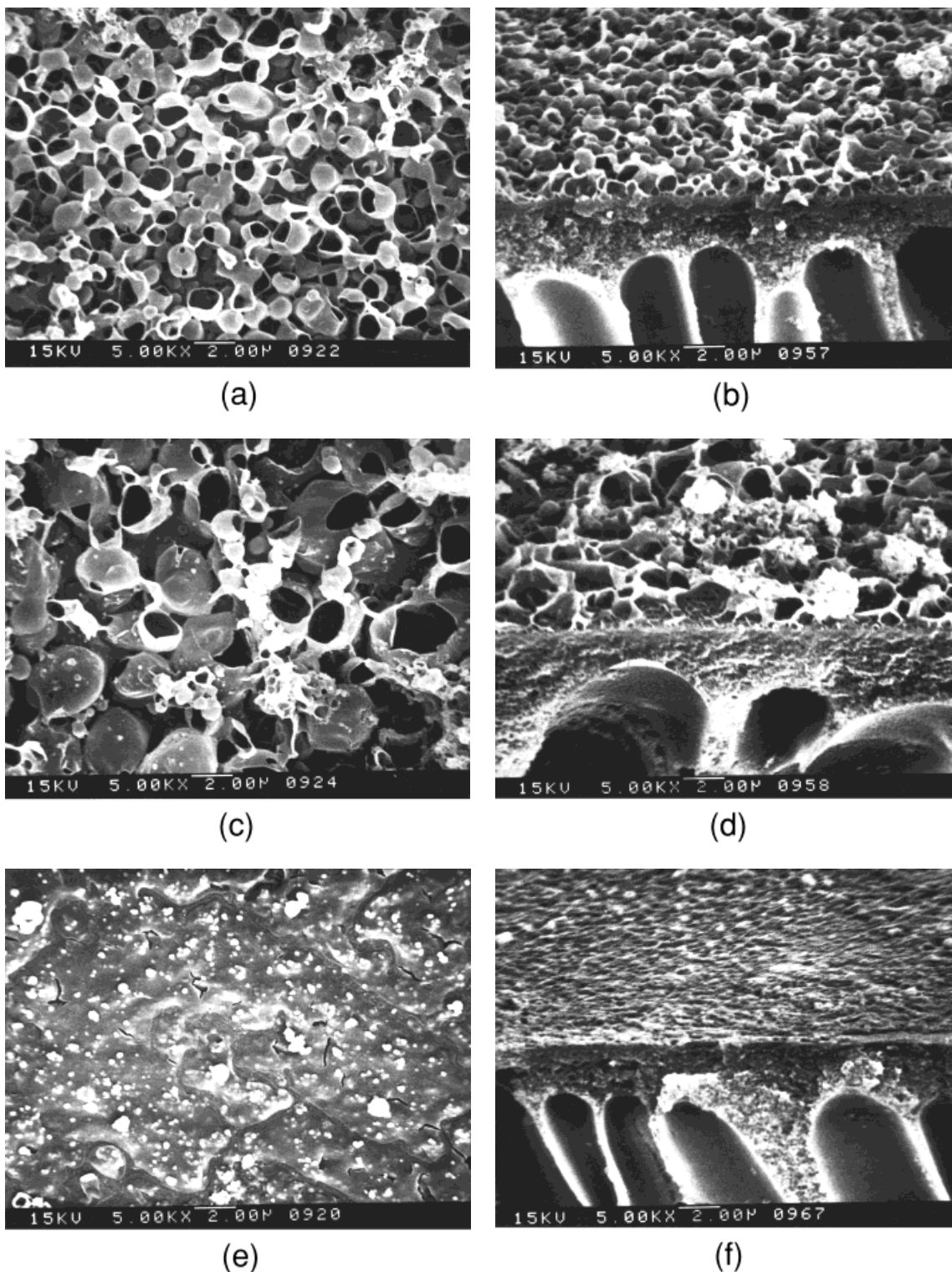
Figure 9 Effect of ethanol volume fraction in aqueous phase on morphologies of the thin-film composite diazoketone membranes. See Table IC for details. Volume ratio of ethanol to water and membrane No.: (a) and (b), 25/75, II-DK-T-E-01; (c) and (d), 50/50, II-DK-T-E-02; (e) and (f), 75/25, II-DK-T-E-03; (g) and (h), 100/0, II-DK-T-E-04. (a), (c), (e), and (g): top views, (b), (d), (f), and (h): edge-on cross-section views.
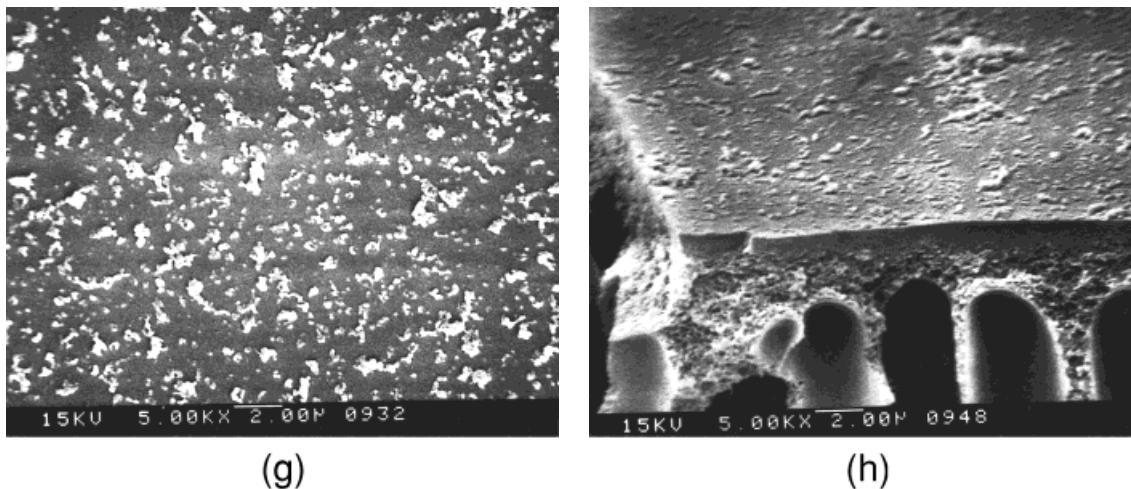
(g)

(h)

Figure 9 (*Continued from the previous page*)

To investigate the effect of surface charge the permeability of the TFC membranes was examined for a series of salts (NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$) in which the charge of the cation and anion were varied systematically. The separation and flux data observed with each of these salts for membranes prepared by interfacial polymerization for 2 h using a CCl_4/acetone solution of the diazoketone **5** with ethanediamine/H_2O and Triton X-114 as a surfactant are summarized in Figure 11. These data are typical of the results obtained with the membranes listed in Table I.

The membrane showed increased separation in the order NaCl < $MgCl_2$ < Na_2SO_4 < $MgSO_4$. However, no stepwise increase in separation was observed when switching solute from monovalent to divalent anion or cation, suggesting that the membrane surface is approximately neutral.

CONCLUSIONS

The work described above clearly demonstrates that it is possible to prepare TFC membranes based on the formation of a polysulfonamide. Dense, relatively flat films are formed at short
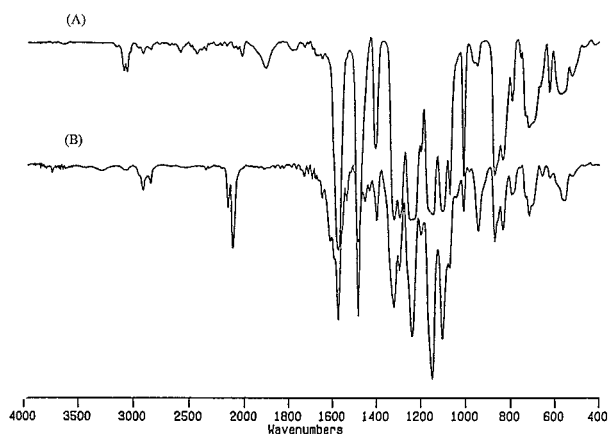

Figure 10 Attenuated total reflectance FT–IR spectra of (A) the support polysulfone membrane and (B) the thin-film composite diazoketone membrane, I-DK-T-01. See Table I for details.
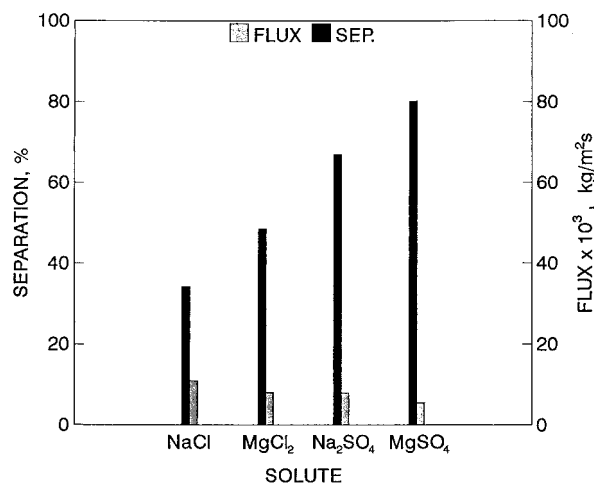

Figure 11 Separation of four inorganic solutes from aqueous solution by a typical thin-film composite diazoketone membrane, II-DK-T-04. See Table I for details. Test conditions: pressure, 6000 kPa; temperature 25°C; feed, 0.17M solute in aqueous solutions.membrane samples.

polymerization times; however, more open, thick films are produced with longer reaction times. The use of water-soluble organic solvents in either the aqueous phase or the immiscible organic phase of the interfacial polymerization seem to improve the properties of the thin film.

A mechanism is proposed that accounts for the formation of open voids on the final membrane surface. These structures could be the result of penetration of the aqueous diamine solution into the forming polymer, engulfment with organic-disulfonylchloride solution, and breaking off of the droplets taking place during the interfacial polymerization. To give salt selectivity, a relatively dense substructure must exist under these surface porous structures. The surface structure is influenced by the presence of surfactants or ethanol in the aqueous diamine solution.

It is also clear from this work that while the NaCl salt rejections of these membranes are not high, and the reaction times are long, the thin films do contain a diazoketone functionality. As such these membranes should be suitable vehicles to probe the impact of photochemical surface modification on the properties of the membranes. The low salt rejections, typical of nanofiltration membranes, and long reaction times are probably related to the relatively slow interfacial reaction rate.

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