

Pervaporation Behavior of Asymmetric Sulfonated Polysulfones and Sulfonated Poly(ether sulfone) Membranes

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ABSTRACT: The sulfonation of polymers and the pervaporation behavior of asymmetric polymeric membranes are described in this study. We confirmed that the sulfonic acid group was successively introduced into the polymer chain by FTIR and ¹H-NMR characterization. The phase diagram indicated that the modified polymer could have water tolerance, implying that the polymer–solvent miscibility was lower. The hyperthin skin layer, suitable for pervaporation, depended on the NMP–DGDE composition, which was important for the fabrication of an asymmetric membrane with high water permeance. The asymmetric membrane exhibited water selectivities equal to or slightly lower than those determined for the dense film. The hyperthin skin layer, which had hardly any defects, was possibly formed by the phase-inversion method. It is obvious that these membranes can be used for the industrial pervaporation process. The permeability and the selectivity of the water–butanol mixture for the asymmetric membranes at 50°C were measured. The permeation rates for water–butanol in the asymmetric membrane were about 80 times greater than those of film, and the separation factor was slightly lower. The NMP–DGDE solvent system might be suitable for a high permeation rate. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 787–798, 2000

Key words: sulfonation; pervaporation; asymmetric membrane; phase inversion

INTRODUCTION

Pervaporation is a process involving the permeation of a liquid through a membrane and the subsequent evaporation of the liquid. This process has been known as a method for separating azeotropic mixtures.^{1,2} Pervaporation has been useful for the concentration of alcohol from dilute aqueous solutions. The membranes for this purpose may be either ethanol permselective or water permselective.³ (Some additional general remarks on polymer choice: It is important the

membrane not swell too much, or the selectivity will decrease drastically. On the other hand, low sorption or swelling will result in a very low flux.)

Pervaporation has been successfully applied to the dehydrating of aqueous alcohol solutions of relatively low water content near their azeotrope point.⁴ This application has been commercially developed with capacities of 2000–150,000 L per day.⁵

The preparation of a membrane with a thinner skin layer is one of the most important factors for achieving a higher permeation rate. It's especially important that the skin layer of a membrane to be used in a gas separation or pervaporation system be as thin as possible and almost defect free in order to obtain a high selectivity and permeation rate.

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For pervaporation, nonporous membranes are required, preferably with an anisotropic morphology—an asymmetric structure with a dense top layer and an open porous sublayer—as found in asymmetric and composite membranes.⁶ There are only a few reports^{7–9} on preparing asymmetric membranes for pervaporation because of the difficulties in finding suitable conditions for their preparation. It is well known that asymmetric membranes have a high permeation rate and mechanical strength due to their structures.¹⁰ The preparation of a new type of asymmetric membrane with a hyperthin skin layer, which has hardly any defects and is less than 100 nm, was developed using a casting solution method. Diethylene glycol dimethyl ether was used as one of the dope solvents to form the skin layer.¹¹

In the present study, in order to develop polymer membranes with a high pervaporation performance, we prepared asymmetric membranes with a hyperthin and defect-free skin layer using polysulfone, sulfonated polysulfone, poly(ether sulfone), and sulfonated poly(ether sulfone).

EXPERIMENTAL

Reagents

Polysulfone [PSf, Udel P-1700 (Amoco, Marietta, OH)] and poly(ether sulfone) [PES, Ultrason (BASF, Ludwigshafen, Germany)] were dried in a vacuum at 130°C for 12 h. Sulfur trioxide (SO₃), triethyl phosphate (TEP), dichloromethane (DCM), and dichloroethane (DCE) were purchased from Aldrich (Milwaukee, WI) and used for sulfonation without purification. For membrane preparation, *N*-methyl-2-pyrrolidone (NMP) and diethylene glycol dimethyl ether (DGDE) were used as solvents. Those solvents were refluxed twice under calcium hydride for purification.

Sulfonating Agents Preparation

A SO₃-TEP (2:1) complex was prepared by dissolving 0.5 mol of SO₃ in 0.25 mol of TEP for 48 h under vigorous stirring.¹² The solution turned to deep red.

Sulfonation

The dried PES (10 g, 0.0431 mol/repeating unit) was dissolved in 50 mL of DCM. An equimolar amount of the SO₃-TEP complex (2:1) was added to the polymer solution. The reaction temperature

and time were fixed as 25°C and 4 h, respectively. Precipitated PES was filtered and dried at 130°C for 12 h.

The dried PSf was also sulfonated in DCE. The sulfonated polymer solution was precipitated into methanol and dried at 130°C for 12 h.

Characterization and Measurements

IR spectra were recorded on a spectrometer; ¹H-NMR spectra were obtained using a spectrometer with DMSO-d₆ as solvent and TMS as the internal standard. Viscosity was measured in 0.5 g/dL NMP solution at 30°C ± 0.1°C with an Ubbelohde viscometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a TA instrument model DSC 2910 and Du Pont model 951, respectively. The DSC run was conducted twice under nitrogen at a heating rate of 20°C/min. TGA experiments were run under nitrogen at a heating rate of 20°C/min. Second-run curves of TGA were considered after a first run of up to 350°C to eliminate absorbed water and small residuals of solvent. The degree of sulfonation was measured via the ion-exchange capacity (IEC) determined by converting the sulfonic acid group to sodium sulfonate with 0.1N NaOH and titrating with 0.1N HCl according to the procedure described by Fisher and Kunin.¹³

Membrane Preparation

Flat-sheet phase-inversion membranes were prepared by casting a polymer solution at 25°C and 65% with a casting knife of 200 μm on top of a polyester nonwoven fabric followed by immersion in an ice-cold water bath.

The polymer solutions were prepared by mixing polymer and solvent mixtures. The solvent mixtures were made by controlling the contents of NMP and DGDE.

Scanning Electron Microscope (SEM)

The membrane cross-section structures were examined by an Oxford SEM. In SEM studies membrane samples were fractured in liquid nitrogen and coated with gold to -150Å.

Cloud Point and Tie Line

Polymer solutions with different compositions (1%, 3%, 6%, 10%, 15%) were placed in tubes at 30°C. In case of polymer solutions with low polymer compositions (1%, 3%), distilled water was

Table I Properties of Polymers

Code	η_{inh} (dL/g) ^a	IEC (meq/g)	T_g (°C) ^b	Decomposition Temperature (°C) ^c		
				T_i (°C) ^d	T_{10} (°C) ^e	T_{max} (°C) ^f
PSf	0.42	0	182	490	510	530
PSf-1	0.46	0.72	213	173	480	505
PSf-2	0.51	1.15	235	157	460	495
PES	0.47	0	223	510	570	590
PES-1	0.50	0.69	240	195	520	550
PES-2	0.55	1.08	260	180	480	500

^a Measured in NMP at a concentration of 0.5 g/dL at 30°C.

^{b,c} Data obtained at a heating rate of 20°C/min in nitrogen.

^d Initial weight loss temperature.

^e 10% weight loss temperature.

^f Maximum weight loss temperature.

slowly added until turbidity occurred. Water–NMP (4:1) was added to other polymer solutions (6%, 10%, 15%) until turbidity occurred.²² The composition at the onset of turbidity, the so-called cloud point, represents the transition concentration between the one-phase and two-phase regions. The cloud point curve can be interpreted as the binodal in a ternary phase diagram.²³

Aliquots of a polymer–NMP–water mixture at its cloud-point composition were kept at 25°C in a thermostatic bath for more than a month. The turbid polymer solutions developed into two clear liquid layers. The less viscous top layer was withdrawn. The water content in this mixture was determined by gas chromatography. The polymer content of the upper phase was determined from the weight after evaporation to dryness. But the top and bottom layers were removed separately and dried for two days until the constant weight of the polymer residue could be observed. Tie-line compositions were then calculated through material balance.^{10,23}

Pervaporation

A pervaporation apparatus¹⁴ was used for measuring the permeation rates of the binary mixtures. The membrane was fixed on a porous stainless-steel plate in a cylindrical pervaporation cell. The effective area of the membrane was 12.7 cm². The feed solution was circulated with a flow rate of 250 mL/min from the feed reservoir in a thermostatic bath and circulated upward from the membrane. Analysis on the feed side as well as on the permeate side was made by using a gas chromatograph. Samples of the permeate were drawn

either from the liquid mixture condensed in the cooling traps or by use of a bypass device in the gaseous phase of the permeate flux. Results were obtained as total fluxed J_{tot} in g/m² h, from which partial fluxes J_i can be calculated according to the relation $J_i = J_{tot} X W_{i,perm}$, where $W_{i,perm}$ is the weight fraction of component i in the permeate. The permselectivity of a membrane was represented by the separation factor (α), defined for a binary mixture as follows:

$$\alpha_{H_2O/BuOH} = \frac{(C_{H_2O}/C_{BuOH})_{permeate}}{(C_{H_2O}/C_{BuOH})_{feed}}$$

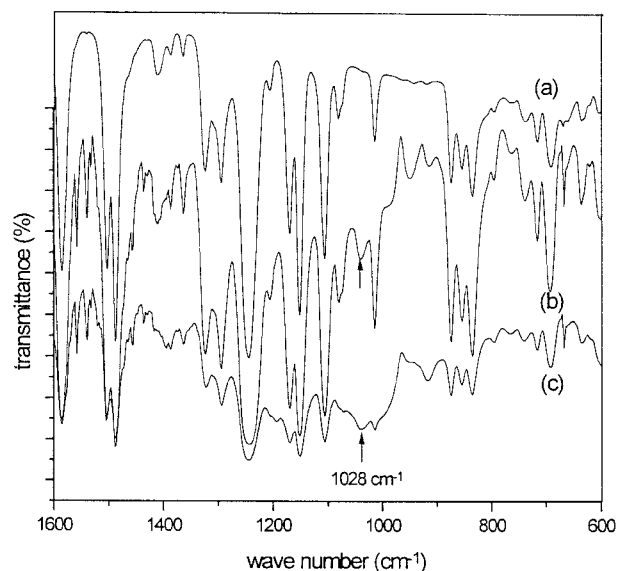


Figure 1 FTIR spectra of (a) PSf, (b) PSf-1, and (c) PSf-2.

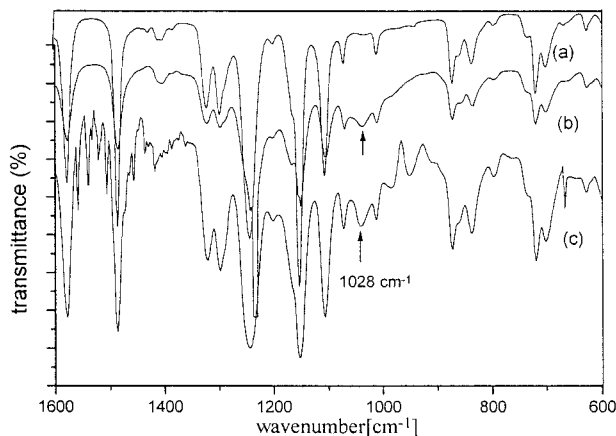


Figure 2 FTIR spectra of (a) PES, (b) PES-1, and (c) PES-2.

where C_{H_2O} and C_{BuOH} are the concentration of water and butanol, respectively.

RESULTS AND DISCUSSION

Sulfonation of Polymers and Their Characterization

PSf and PES were sulfonated with a 2:1 SO_3 -TEP complex. The results of IR and 1H -NMR showed that the sulfonate group was introduced successfully. This is in good agreement with results described in literature.^{12,15,16} The reaction PSf solution was added over 1 h to an excess amount of vigorously stirred methanol. The precipitated

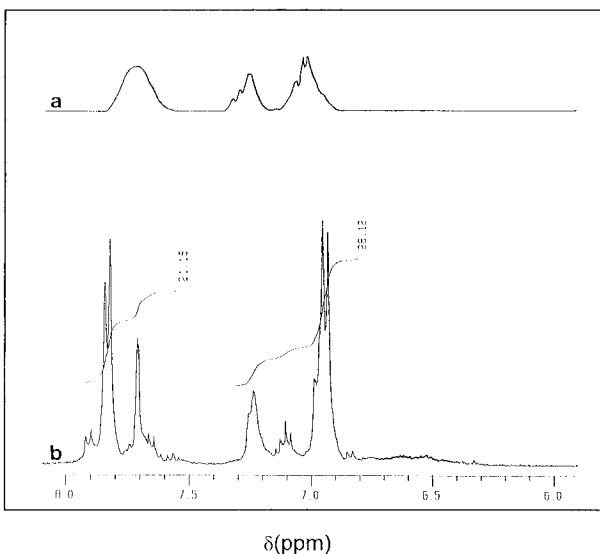


Figure 3 1H -NMR spectra of (a) PSf and (b) PSf-1.

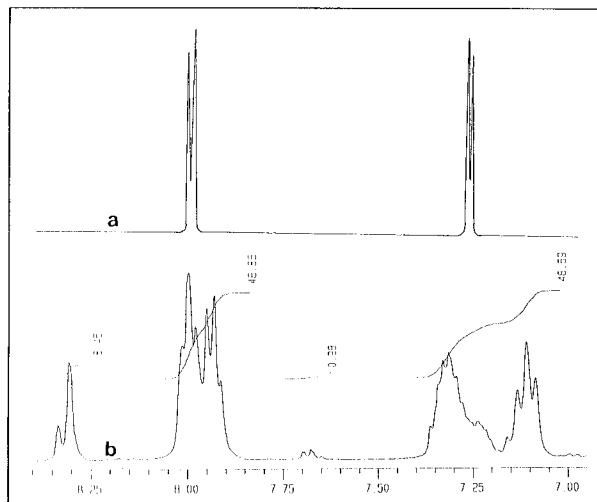


Figure 4 1H -NMR spectra of (a) PES and (b) PES-1.

polymer was washed with methanol and dried in a vacuum at $80^\circ C$ overnight. However, sulfonated PES was in a very fine slurry during the reaction. Therefore, the sulfonated PES was filtered and dried directly. The degree of sulfonation was measured quantitatively via the IEC. The IEC with

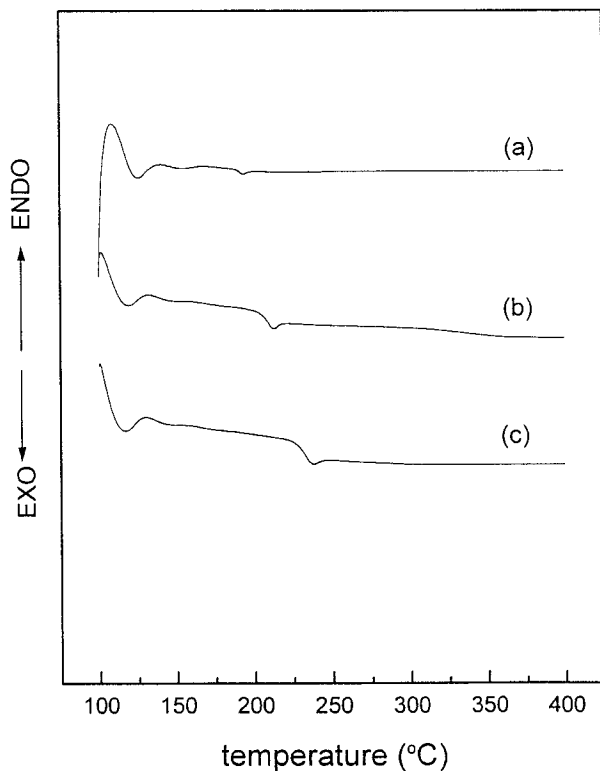


Figure 5 DSC traces of (a) PSf, (b) PSf-1, and (c) PSf-2.

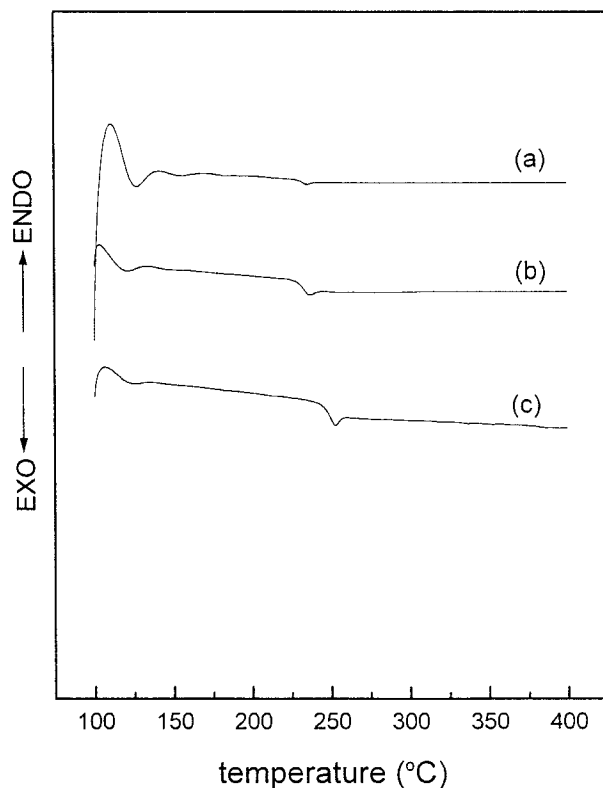


Figure 6 DSC traces of (a) PES, (b) PES-1, and (c) PES-2.

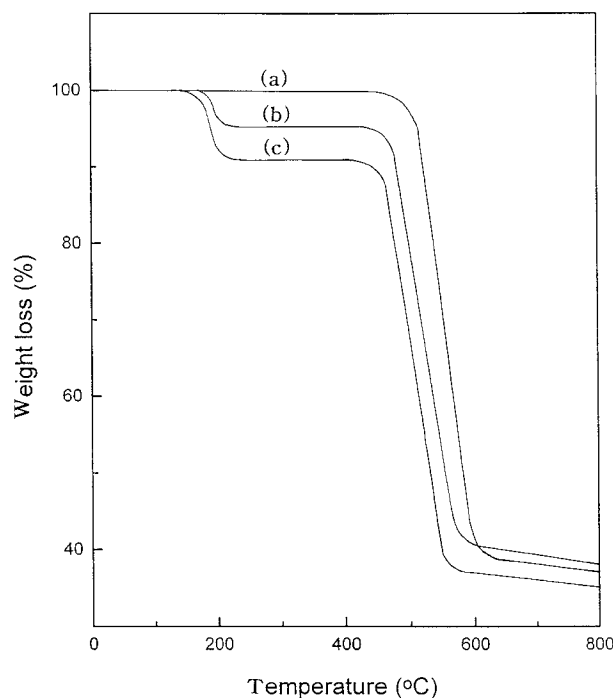


Figure 7 TGA curves of (a) PSf, (b) PSf-1, and (c) PSf-2.

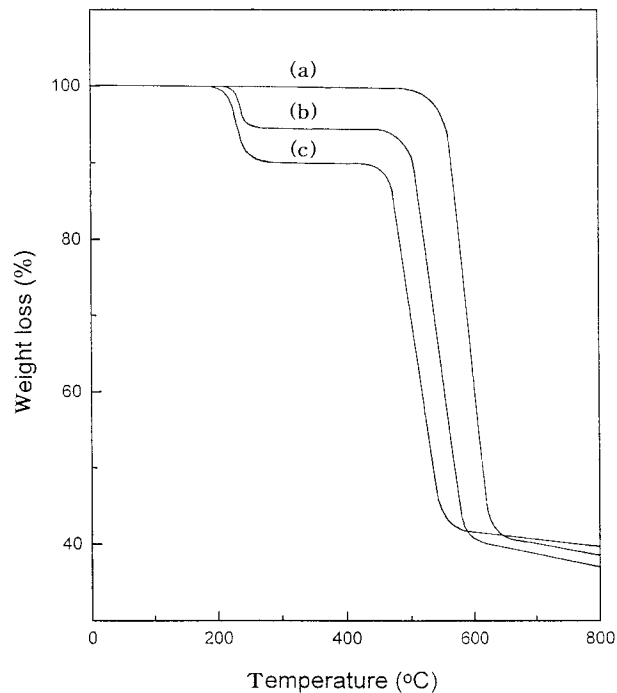


Figure 8 TGA curves of (a) PES, (b) PES-1, and (c) PES-2.

the values determined experimentally by acid-base titration and inherent viscosity are compared in Table I. IEC values for nonsulfonated PSf and PES were zero and took on the role of a control. It is important to emphasize that sulfonated PSf and PES had inherent viscosity values equal to 0.51 and 0.55 dL/g, which were greater than those of nonsulfonated PSf and PES, respectively. These results indicate that the original polymers were not degraded by a sulfonating agent. However, in TGA studies with increasing IEC values, maximum weight-loss temperatures were slightly lowered. If sulfonated polymers were not degraded, the TGA curve would exhibit a similar pattern to the original polymers at the second-stage degradation. In Figures 1 and 2, FTIR shows the typical absorption peak at 1028 cm^{-1} . This peak identifies the asymmetric sulfonated group. Figures 3 and 4 show the $^1\text{H-NMR}$ spectra of sulfonated polymers. The sulfonic acid group causes a significant downfield shift of the aromatic hydrogens. In the case of PSf and sulfonated PSf, the proton attached to the aromatic group at 7.25 ppm was shifted downfield to 7.85 ppm. For PES and sulfonated PES, the proton attached to the aromatic group of 7.28 ppm was shifted downfield to 8.30 ppm. This downfield shift is attributed to the attachment of the elec-

Table II Compositions of Casting Solution and Solubility Properties

Code	Cosolvents (NMP/DGDE) ^b					
	10/0	8/2	6/4	4/6	2/8	0/10
PSf ^a	O	O	O	O	O	X
PSf-1	O	O	O	O	O	X
PSf-2	O	O	O	O	O	X
PES	O	O	O	O	X	X
PES-1	O	O	O	O	O	X
PES-2	O	O	O	O	O	X

^a The composition of polymer/cosolvent is 23/77 (wt %).

^b O, soluble at room temperature; X, insoluble.

tron-withdrawing sulfonic acid group to the aromatic carbon.

The thermal behaviors of these sulfonated polymers were examined using both DSC and TGA. Figures 5 and 6 confirm that the introduction of sulfonic acid groups to the aromatic carbon that forms hydrogen bonds increases the T_g of sulfonated polymers with increasing IEC. This T_g increase can be explained by the reduction of rotational freedom around the polymer main chain due to the sulfonic acid group. The TGA curves in nitrogen (Figs. 7 and 8) exhibited a two-stage degradation process. Sulfonated polymers showed a similar behavior, characterized by first decomposition at 180–230°C. The second decomposition behavior was similar to the original polymers. This pattern may be attributed to decomposition of sulfonic acid groups: the observed first weight loss increases with an increase in IEC of the polymer. The maximum weight-loss temperature was relatively similar with increasing degree of sulfonation. These facts are summarized in Table I.

Membrane Preparation for Pervaporation

For the pervaporation or gas separation to be successful, a membrane with a high selectivity and permeance is required. To minimize the thickness, an asymmetric membrane is preferred, with a defect-free ultrathin skin layer to retain intrinsic selectivity and a porous substructure to support the skin layer.^{17,18} The phase-separation method is the most widely used technique for fabricating the asymmetric membranes, and the membranes are prepared by controlled phase separation of polymer solutions into two phases, one with high polymer concentration and one with low polymer concentration.^{19,20} H. Hachisuka et al.²¹ reported diethylene glycol dimethyl ether (DGDE) used as a solidification solvent could form the hyperthin skin layer with hardly any defects. They used polyimide as a polymer, and the cross-section morphology was spongelike. Though it is a different kind of polymer, DGDE could be used as a cosolvent with NMP in our work.

Table III Separation Factor and Flux of Water–Butanol^a through Film and Asymmetric Membranes

Code	Separation Factor (α)					Flux (kg/m ² hr $\times 10^2$)				
	Film ^b	8/2	6/4	4/6	2/8	Film ^b	8/2	6/4	4/6	2/8
PSf	37	18	23	32	36	0.054	2.95	2.72	2.69	2.65
PSf-1	54	21	35	49	52	0.068	3.20	3.13	2.85	2.91
PSf-2	72	45	52	65	68	0.085	3.24	3.12	2.93	2.91
PES	58	36	41	54	—	0.061	3.13	2.98	2.81	—
PES-1	67	34	45	62	65	0.071	3.12	3.05	2.79	2.73
PES-2	95	42	53	87	91	0.084	3.45	3.33	3.17	3.15

^a Feed: 90% by weight butanol; feed temperature: 50°C.

^b Film thickness: 50 μ m.

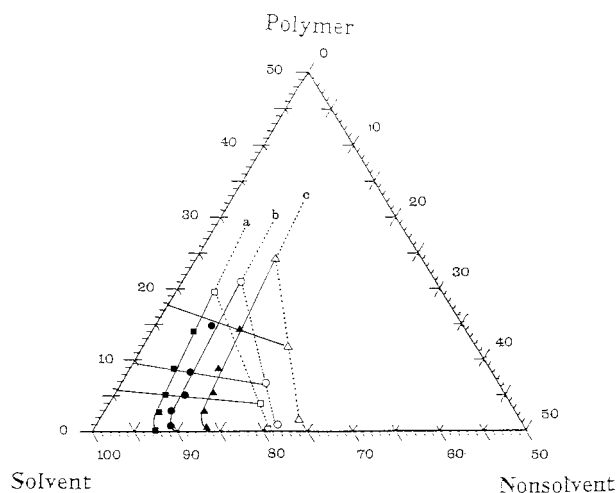


Figure 9 Polymer precipitation curves of (a) PSf, (b) PSf-1, and (c) PSf-2 with NMP solvent at 30°C.

To make a suitable pervaporation membrane with high permeance, DGDE was used as cosolvent. The solvent compositions used in this study are shown in Table II. DGDE was not a solvent but a swelling agent for these polymers (PSf, PES, sulfonated PSf, and sulfonated SPES). Therefore, NMP and DGDE mixtures of different weight ratios were used as solvents. All the polymers except PES were soluble in the solvent composition of NMP–DGDE (2:8). To find the composition of a solvent mixture, a pervaporation experiment was done. The feed solution used was butanol (95% by weight). The permeate flux and permselectivity represented by a separation factor were collected in Table III.

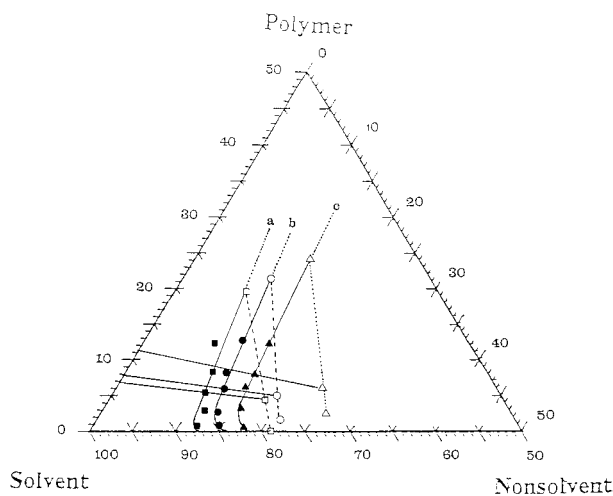


Figure 10 Polymer precipitation curves of (a) PES, (b) PES-1, and (c) PES-2 with NMP solvent at 30°C.

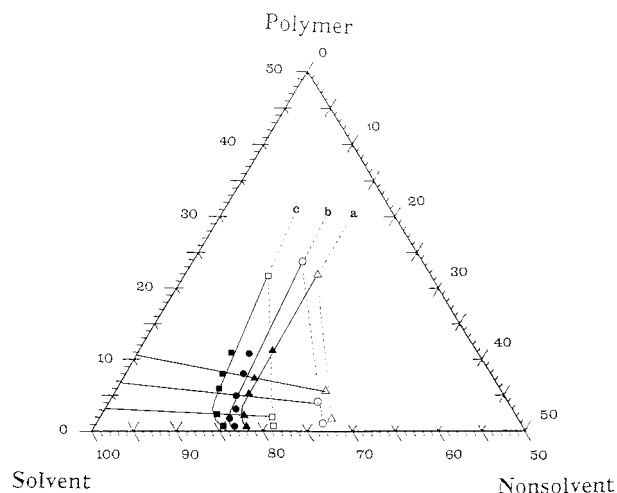


Figure 11 Polymer precipitation curves of PES-2 (a) NMP–DGDE = 10:0, (b) NMP–DGDE = 4:6, and (c) NMP–DGDE = 2:8 with NMP–DGDE cosolvent at 30°C.

Pervaporation

The separation of water–butanol mixtures through various glassy polymeric membranes was evaluated to investigate the sulfonation and the DGDE effect. Since this study focused on the selective removal of water from alcoholic mixtures, the purpose of the sulfonation was to choose a polymer material with a higher affinity for water than that of unmodified polymers.

The separation factors and the permeation rates for the butanol (95% by weight) through both the unmodified and the modified polymers are presented in Table III for an operating temperature of 50°C. As can be seen from the data of various films, with increasing IEC, the separation factors increased. We can infer from this that the polymer chains of the membranes contain very hydrophilic polar groups, namely, sulfonate groups. As expected, it was observed that the sulfonated polymers have higher water-selective properties compared to those of unmodified polymers. The modified membranes were preferentially permeated by the water; hence they were more selective for the water from the water–butanol mixtures than for the butanol alone. In addition, the permeation rates are somewhat higher for the sulfonated membranes than for the unmodified ones.

To increase membrane performance, an asymmetric membrane with a hyperthin skin layer was prepared. Table III also shows the effect of the DGDE in the casting solution. By using the DGDE in the casting solution, the water perme-

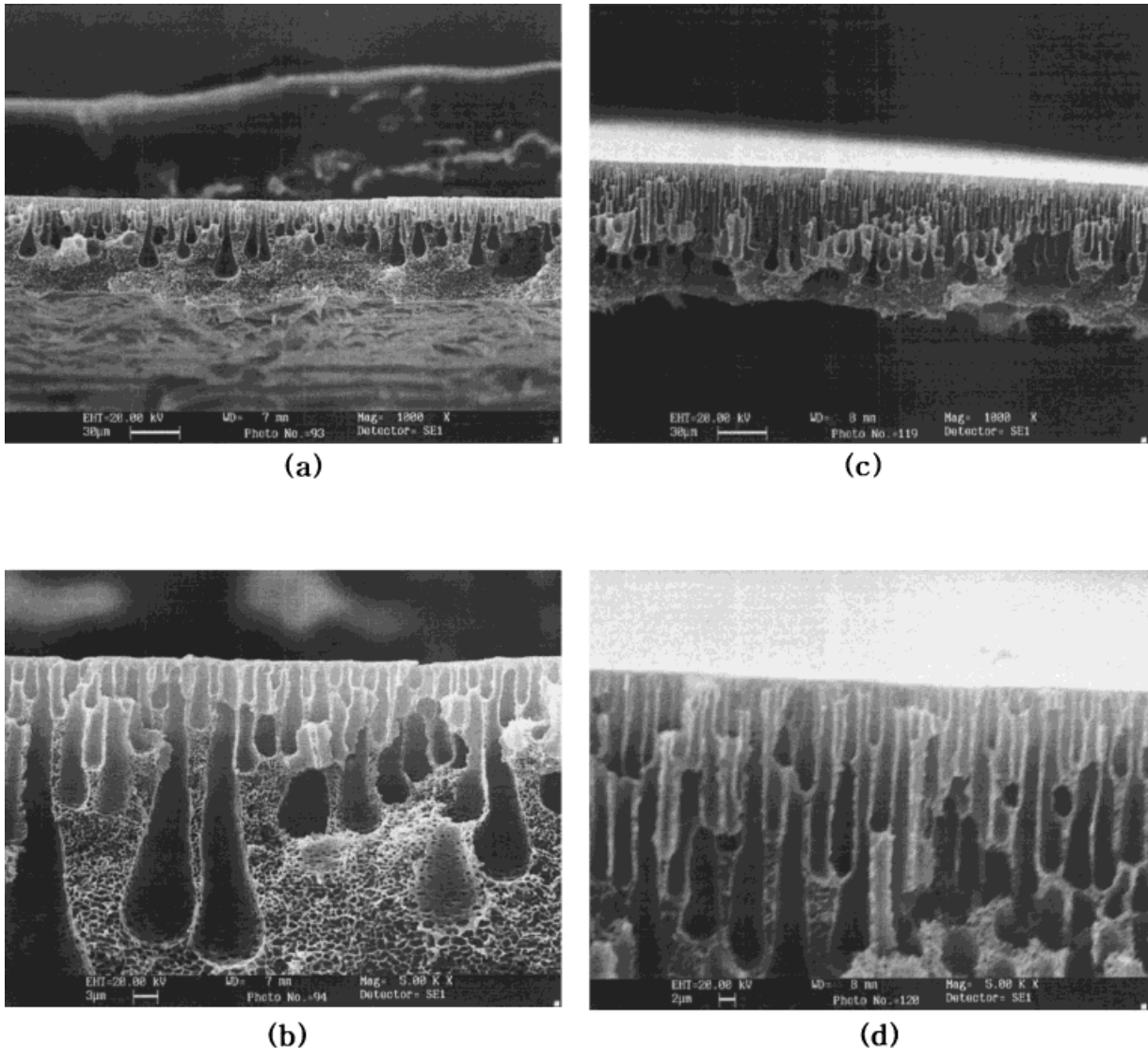


Figure 12 SEM photographs of effect of DGDE in 23 wt % PES-2 membrane preparation: (a) cross section in NMP, (b) top layer in NMP, (c) cross section in NMP-DGDE = 8:2, (d) top layer in NMP-DGDE = 8:2, (e) cross section in NMP-DGDE = 4:6, (f) top layer in NMP-DGDE = 4:6, (g) cross section in NMP-DGDE = 2:8, and (h) top layer in NMP-DGDE = 2:8.

ation rates were about 80 times larger than those determined in the film. The selectivities of the asymmetric membranes were greater compared to those of the dense membrane, without the necessity of an additional coating process. This result indicates that the organic vapor transport through the asymmetric membranes is predominantly carried out by a solution-diffusion mechanism and that the surface skin layer is essentially defect free. With increasing content of DGDE, the selectivities were largely increased, and permeation rates were decreased. Though we

could not confirm the possibility for pervaporation in SEM observation, the pervaporation test showed that by adding DGDE to the polymer-NMP solution, a hyperthin and defect-free skin layer was formed.

As a result, contents of 4:6 and 2:8 of NMP-DGDE are expected to be used for pervaporation. However, in the case of 8:2 and 6:4, we expect that these membranes will be more suitable for nanofiltration than for pervaporation. More studies about suitability for nanofiltration will be presented in a future publication.

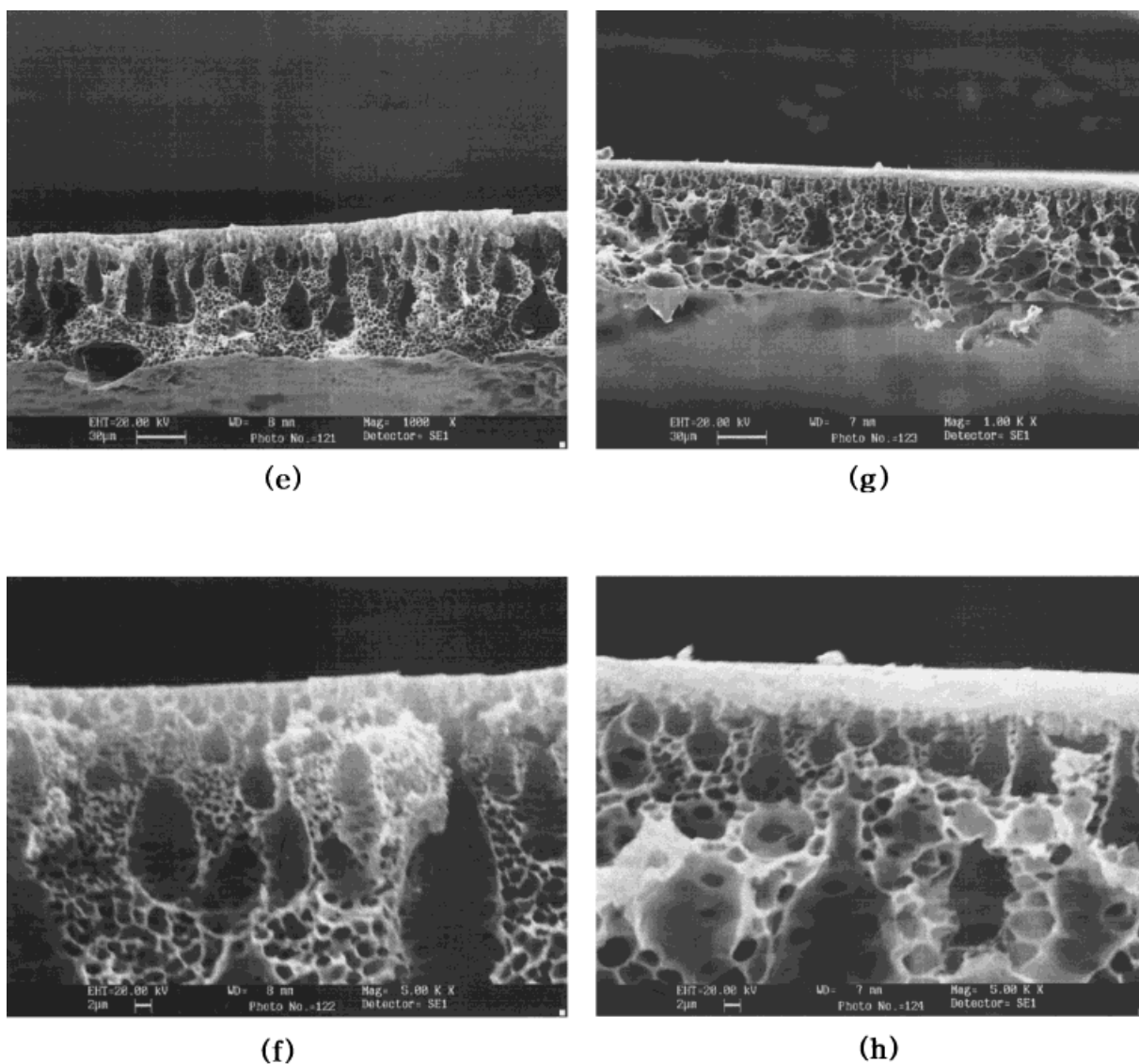


Figure 12 (Continued from previous page)

Phase Diagram

The polymer cloud-point data indicate the degree of tolerance for water by the unmodified and the modified polymers in the miscibility regions. They also attest to the capacity of the polymers to associate with water. Figures 9 and 10 clearly show that the miscibility region of sulfonated polymers, which are more hydrophilic, are wider compared to those of the unmodified polymers. Figure 11 shows the DGDE effect with the PES on the cloud points. By increasing the composition of the DGDE from 20 to 80% by weight, the size of the miscibility region, which reflects the amount of nonsolvent to be imbibed by

the polymer, is smaller. Other polymers showed similar patterns. The amount of water imbibed in the precipitation step appeared to have a significant influence on the pore structure in the top layer of the membrane and the polymer morphology in the resulting membrane.

Membrane Morphology by Phase Separation

Asymmetric membranes were prepared using a polymer–NMP–DGDE solution. The cross-section structures of the membranes using SEM are shown in Figures 12 and 13. As can be seen in Figure 12, membranes prepared from NMP [Fig. 12(a,b)] and NMP–DGDE (8:2)[Fig. 12(c,d)] do not

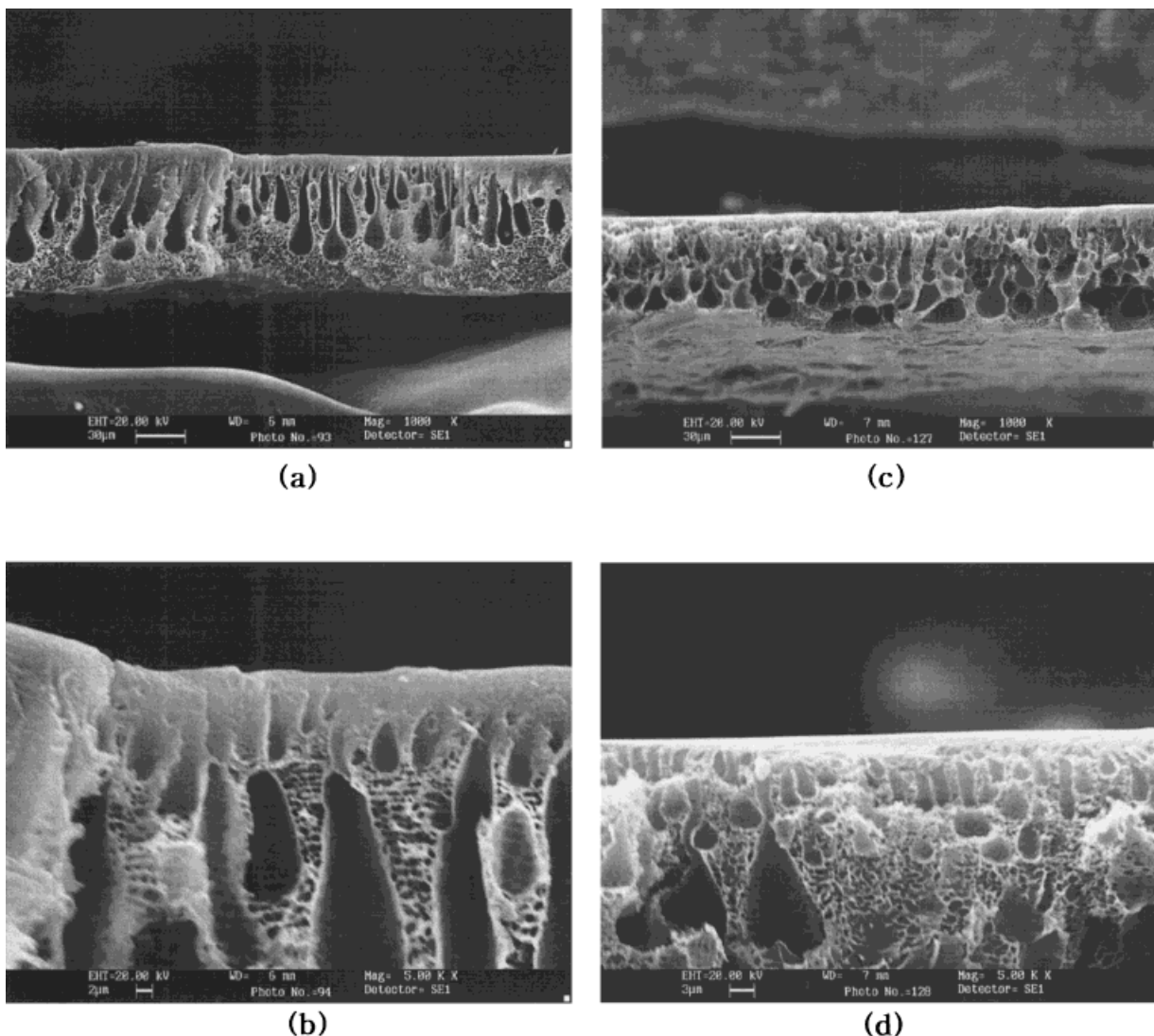


Figure 13 SEM photographs of membranes prepared from 23 wt % polymer and NMP–DGDE = 4:6 casting solutions: (a) cross section of PES membrane, (b) top layer of PES membrane, (c) cross section of PES-1 membrane, (d) top layer of PES-1 membrane, (e) cross section of PSf membrane, (f) top layer of PSf membrane, (g) cross section of PSf-1 membrane, (h) top layer of PSf-1 membrane, (i) cross section of PSf-2 membrane, and (j) top layer of PSf-2 membrane.

have enough skin layer and have straight finger voids. However, if the DGDE compositions is larger [Fig. 12(e–h)], the skin layer is forming. Moreover, a spongelike porous matrix is shown. As a result, the morphology of the asymmetric membrane using NMP–DGDE (4:6 and 2:8) cosolvents consisted of a hyperthin skin layer and finger voids and a spongelike porous matrix. For pervaporation, NMP–DGDE (6:4) is suitable. Therefore, Figure 13 shows SEM photographs of all the membranes prepared from the cosolvent of NMP–DGDE (6:4). All the SEM photographs have

similar patterns. Interface between skin layer and support layer can be observed. And finger voids are lowered. Instead, a spongelike structure is shown. With an increase in IEC [Fig. 13(c,d,g,h,i,j)], large finger voids are changed into small voids. As is known in triangular-phase diagrams, the polymer–polymer miscibility is lowered with an increase in IEC. These result in faster liquid–liquid demixing, which is the cause of additional formation of a thin skin layer. Adding the DGDE to the casting solution causes the precipitation curve to shift to the right of the axis.

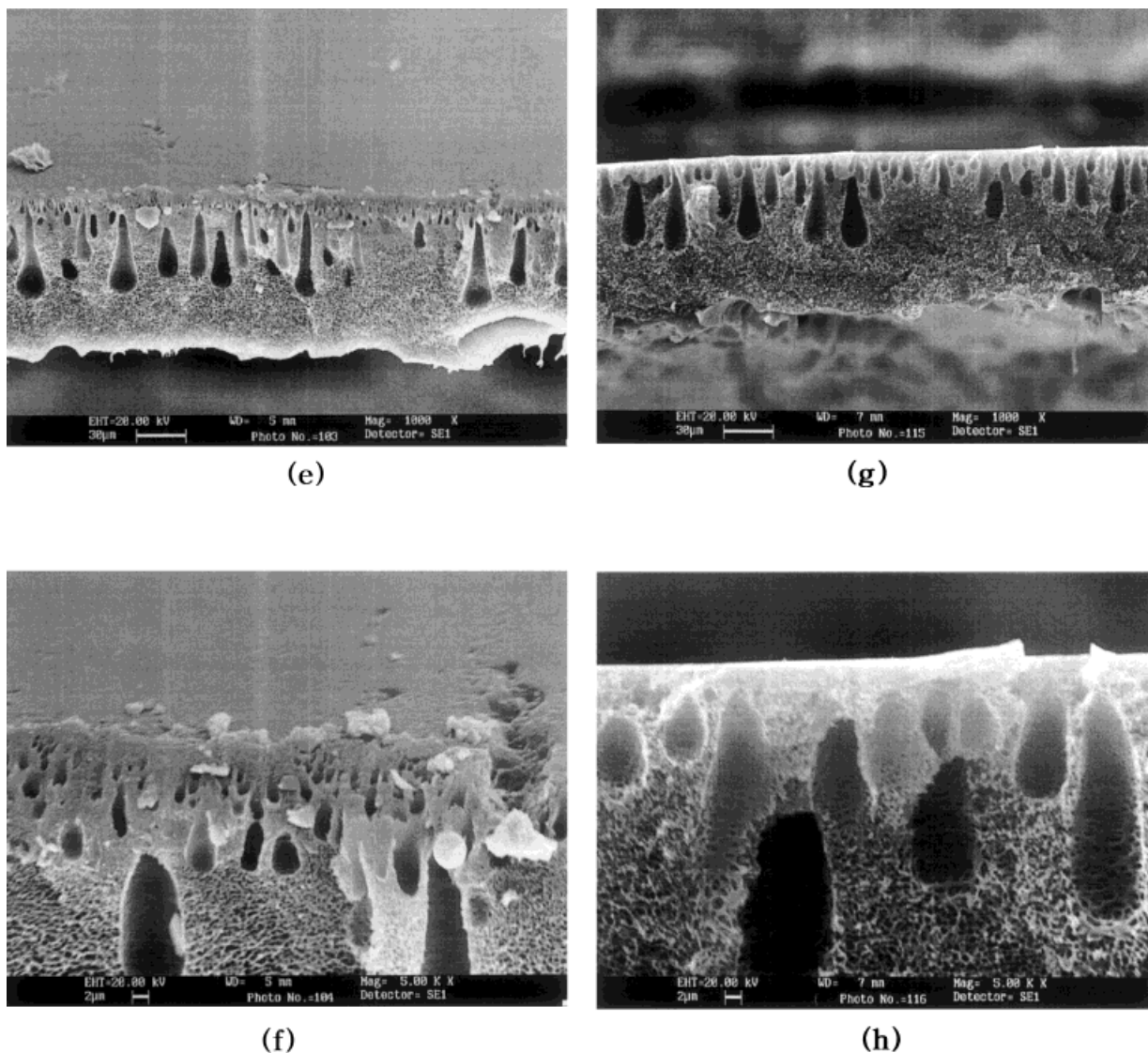


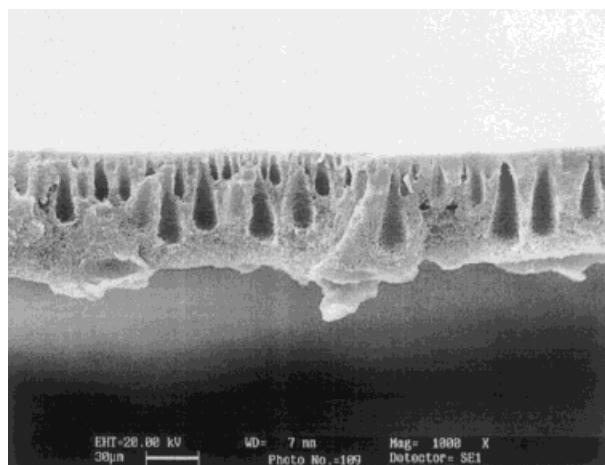
Figure 13 (Continued from the previous page)

This means that the polymer–polymer miscibility is higher. The higher polymer–polymer miscibility makes a solvent exchange with nonsolvent difficult. This causes the formation of a much thicker skin layer, which indicates that these membranes may be used for pervaporation. However, until the pervaporation experiments were performed, we could not confirm that only these morphologies were suitable for pervaporation. The approximately 80 times permeation rate increase is due to the hyperthin skin layer as can be shown by SEM observation. Therefore, the membrane performance, especially permeation rate, is better compared to that of film. The skin layer was hyperthin and defect free in the SEM obser-

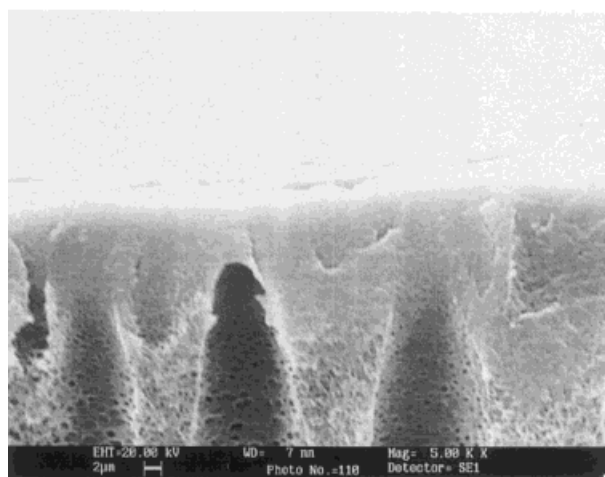
vation. Though the skin layer and porous matrix were formed as one body, the interface was clear. By increasing the DGDE content in polymer solution, macrovoids were reduced, and instead spongelike structures were gradually formed. These phenomena were similar in all membranes of our work.

CONCLUSIONS

In this work we have investigated the role played by DGDE in preparing asymmetric pervaporation membrane with unmodified polymers and sulfonated polymers. Moreover, thermally stable PSf



(i)



(j)

Figure 13 (Continued from the previous page)

and PES were sulfonated in a solution process and a slurry process, respectively. Unmodified polymers and sulfonated polymers with good pervaporation performance were fabricated by the dry-wet phase-inversion method. The membrane prepared by the phase-inversion process consisted of a defect-free and hyperthin layer, which is suitable for pervaporation.

By controlling the DGDE composition, it was possible to prepare an asymmetric pervaporation membrane with a hyperthin layer. With an increasing content of DGDE, the separation factor was close to that of the dense film. NMP-DGDE compositions, which are suitable for water-buta-

nol pervaporation, were 4:6 to 2:8. The larger selectivity in the membrane appears to be responsible for the more packed structure in the skin layer. However, the permeation rate is about 80 times greater compared to that of the dense film. The sulfonated polymers could tolerate more water, as was confirmed in the phase diagram. Sulfonated polymers prepared by a $\text{SO}_3\text{-TEP}$ complex had greater selectivity than did PSf and PES.

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