Preparation of Newly Asymmetric Polyimide Membranes by Phase Inversion

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SYNOPSIS

This study was undertaken to prepare and characterize the newly asymmetric polyimide membranes by using the phase inversion technique. They were performed in ultrafiltration. The casting solution was prepared from the conventional method and the newly developed one. The latter was that the solution was directly prepared from a polyimide solution, which was yielded by the one-step polymerization. The membranes were prepared under several conditions to investigate their separation process. All the membranes have exhibited outstanding chemical stability as well as excellent performance because polyimides as membrane material have shown good solubility, excellent chemical stability, and outstanding thermal property. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Filtration, one of the most important processes in the various industries is defined as the separation of two or more compounds from a fluid by passing the mixture through a functional barrier.[1,2] Membrane filtration, which is a type of filtration, extends its application further to include the separation, concentration, and filtration.[3-6] The important role of a membrane is to act as a selective barrier. It should permit passage of certain compounds and retain other compounds of a mixture. In the practical application, either the permeating stream or the retained phase should be enriched in specified compounds.

Membranes for pressure-driven separation processes can be divided into various separation processes based on the particle or molecular size[7-9]: microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), or hyperfiltration (HF), etc. The nature of those membranes could be controlled by the size of the permeated components and the pore size of membranes.

Membranes have some limitation in application. In HF process, it is frequently the osmotic pressure of the concentrated solute that limits the process. In the case of UF process, it is rarely the osmotic pressure of the retained macromolecules but rather the low mass transfer rates associated with concentrated and viscous macromolecular solution with increasing viscosity. Other problems are the fouling of membranes, the poor cleaning of modules, and the restricted operating conditions.

Recently, some of those problems have been overcome through the development of superior membrane materials and improved module design.[10-12] The results have vastly enlarged the application of membrane process.

The objective of this paper is the preparation of the newly asymmetric polyimide membranes by using phase inversion technique. Specially, the dope solutions were prepared from the conventional method and the newly developed one. The latter was that the dope solution was directly prepared from the polyimide solution via one-step polymerization from monomers.

EXPERIMENTAL

Materials

Polyimide (PI) derivatives, which were synthesized by the one-step polymerization in our laboratory, were used as membrane materials. Their chemical

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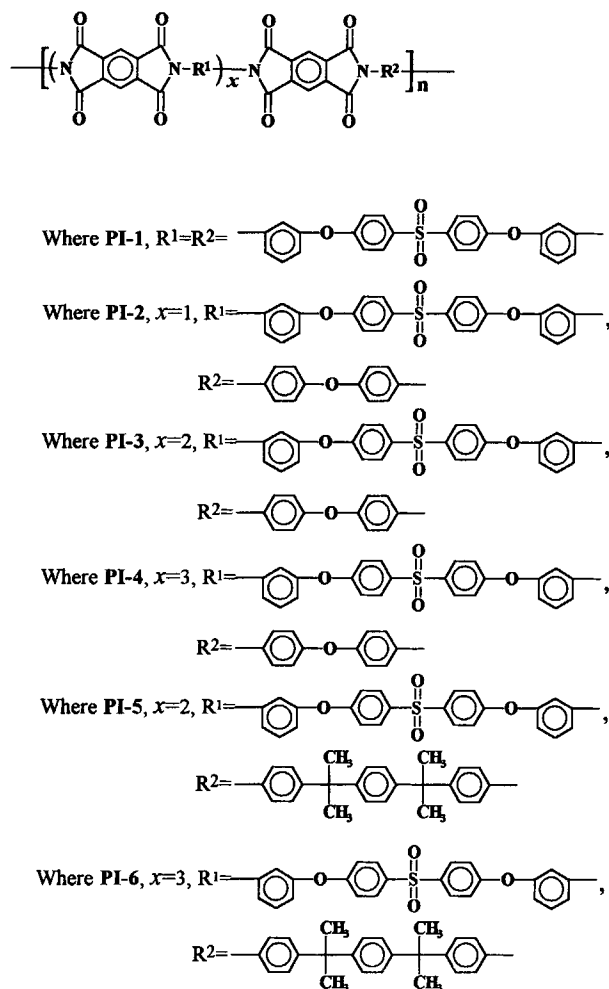
Figure 1   Molecular structure of the polyimides synthesized.

structures and properties are described in Figure 1 and Table I, respectively. The synthesized PIs had good solubility in some solvents such as 1-methyl-2-pyrrolidone (NMP), N,N'-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), m-cresol, and

so on.

Polyvinylpyrrolidone (PVP, MW 1 × 10⁴, Aldrich Chemical Co.) and polyethyleneglycol (PEG, MW 6 × 10³ ~ 5 × 10⁴, Aldrich Chemical Co.) were dried under reduced pressure before use.

1-Methyl-2-pyrrolidone (NMP) and dichloromethane (DCM) were obtained from Aldrich Chemical Co. and used without further purification.

Preparation of PI Membranes

All the membranes were made by the wet process method. Figure 2 is a schematic diagram showing a general procedure for preparing the flat sheet membrane. Figure 3 illustrates the newly developed one. In the newly developed procedure, the dope solution could be directly prepared via one-step polymerization from a dianhydride and a diamine.

The dope solution consisted of the polymer, solvent, and additive with the specific composition. Membranes were hand cast on the nonwoven polypropylene fabric at 25°C, RH 65 ± 2% in the thermohydrostatic chamber. The casting thickness was in the range of 150–300 μm. The casting speed was about 5 cm/s, and the solvent evaporating period before immersion into the coagulating medium was 30 s. Phase inversion was performed by immersing the cast membrane into water bath at 0–4°C for 6 h, then the membrane was washed with water in room temperature for 48 h.

Evaluation of Membrane Performance

The characteristics of the membrane performance was determined by evaluating the pure water flux (PWF) and solute retention (SR). PWF and SR were calculated from the eqs. (1) and (2), respectively.

The solute concentration in the feed and the permeate solutions was measured with high-pressure liquid chromatography (HPLC) differential refrac-

Table I   The Properties of PIs Synthesized

PI No.	Viscosity (dL/g)[a]	Tg (°C)[b]	Ti (°C)[c]	Solubility[d]
PI-1	0.79	245	400	++
PI-2	0.44	290	430	++
PI-3	0.43	280	450	+
PI-4	0.43	264	400	+
PI-5	0.67	270	420	+
PI-6	0.63	260	420	+

[a] Measured at the concentration of 0.5 g/dL polyimide in NMP at 30°C.
[b] Observed by DSC at a heating rate of 10°C/min in air.
[c] Initial weight loss temperature measured thermogravimetric analysis at a heating rate 20°C/min in air.
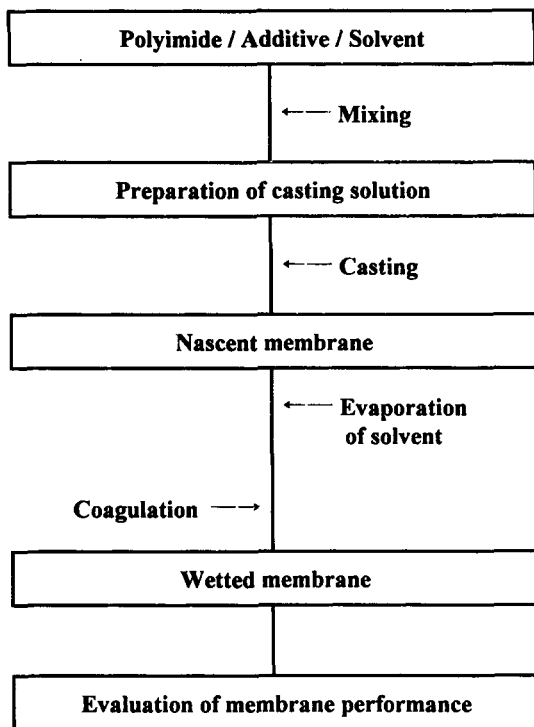[d] Solubility: (++) very good and (+) good in NMP at 25°C.

Figure 2   The most conventional experimental procedure.

tometer (Waters 410). The applied operating pressure was 1 kgf/cm^2. All the evaluation experiments were carried out at 25°C in a thermostatic chamber.

PWF(L/m^2 h)

$$= \frac{\text{Volume of permeated water (L)}}{\text{Effective area (m}^2) \times \text{time (h)}} \quad (1)$$

$$SR(\%) = (1 - C_p/C_f) \times 100 \quad (2)$$

where, C_p is solute concentration in permeate solution, and C_f is the solute concentration in feed solution.

The membrane structure was investigated by scanning electron microscopy (SEM; AKASHI-DS-130). The residual water within the samples was removed completely by freeze-drying, then the samples were coated with gold under high vacuum. The cross sections of membranes were observed from the fractured sample.

RESULTS AND DISCUSSION

Table II shows the results on the performance of PI-1 membrane prepared with different polymer concentrations ranging from 16 to 25% (w/w) in

NMP. All the membranes were cast with 200 μm thickness and prepared under the same conditions. From the results, the PWF tended to decrease, while the SR increased with increasing PI contents in the casting solution. Especially, above 20% (w/w), the membrane exhibited up to about 85% of SR for PEG 20,000. It means that increasing the PI contents in the casting solution leaded to a higher polymer concentration at the upper layer. This implied that the dense upper layer of membrane was formed by increasing the polymer contents.[9]

Table III shows the PWF and the SR of PI-1 membrane prepared from the newly developed method. In the method, the dope solution was directly produced from the one-step polycondensation of dianhydrides and diamines. The PWF and the SR of both PI-1 membranes prepared from the different method were about the same.

Table IV exhibits the typical PWF and SR of PI-1 membrane with different casting thickness. The PWF was decreased with increasing thickness of cast membranes. This behavior might relate to the tortuous effect. Tortuosity was enlarged in the
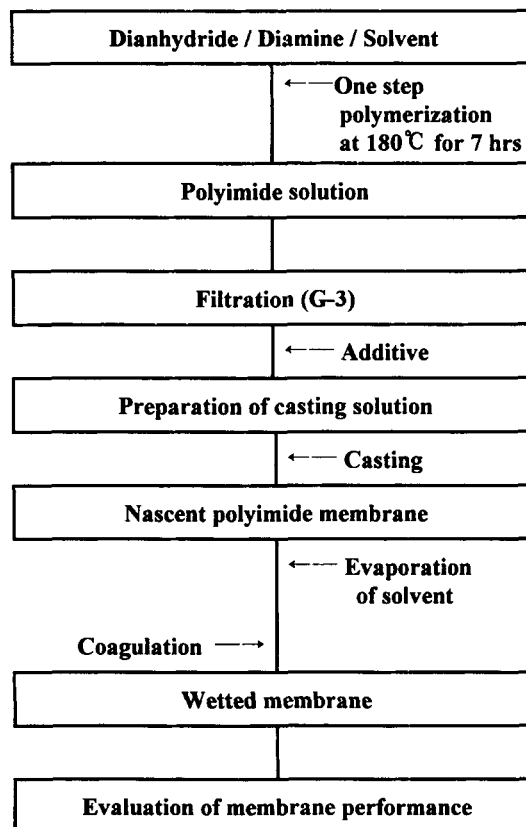

Figure 3   Experimental procedure of the newly developed method.

Table II   Typical Water Flux and Solute Retention of PI-1 Membrane With Different Polymer Concentrations[a]

PI Conc. (wt %)	PWF[b] (L/m² h)	Solute Retention (%)[c]			
		10,000	20,000	35,000	50,000
16	320	13	30	50	> 97
18	262	33	67	83	> 97
20	230	47	77	88	> 99
23	184	60	85	93	> 99
25	130	60	92	97	> 99

[a] Casting conditions: solvent, NMP; solvent evaporation period, 30 s; solvent evaporation temp, 25°C; RH, 65%; casting thickness, 200 μm.
[b] Applied operating pressure: 1 kgf/cm².
[c] Feed solution: 1000 ppm PEG aqueous solution.

Table III   Typical Water Flux and Solute Retention of PI-1 Membrane Prepared by Different Methods[a]

PI Conc. (wt %)	PWF (L/m² h)	Solute Retention (%)			
		10,000	20,000	35,000	50,000
23[b]	184	60	85	93	> 99
25	130	60	92	97	> 99
23[c]	180	62	87	92	> 99
25	120	57	91	97	> 99

[a] Casting and evaluation conditions were the same as in the preceding case.
[b] Membrane was prepared from the conventional method.
[c] Membrane was prepared from the newly direct method.

Table IV   Typical Water Flux and Solute Retention of PI-1 Membrane With Different Casting Thickness[a]

PI Conc. (wt %)	Thickness (μm)	PWF (L/m² h)	Solute Retention (%)			
			10,000	20,000	35,000	50,000
23	150	200	20	75	90	> 95
	200	180	62	87	92	> 99
	250	133	57	91	97	> 99
	300	105	58	93	97	> 99

[a] Casting and evaluation conditions were the same as in the preceding case. Membrane was prepared from the newly direct method.

Table V   Permeation Characteristics of PI-1 Membrane With Different Contents of PVP[a]

PI Conc. (wt %)	PVP Contents[b] (wt %)	PWF (L/m² h)	Solute Retention (%)			
			10,000	20,000	35,000	50,000
23	0	180	62	87	92	> 99
	10	200	11	65	78	> 99
	20	250	0	30	55	92
	30	330	0	10	37	92
	50	450	0	0	20	90

[a] Casting and evaluation conditions were the same as in the preceding case. Membrane was prepared from the newly direct method.
[b] PVP contents was wt % against PI weight.

Table VI   The Effect of NMP/DCM Mixed Solvent System in Dope Solution on the Permeation Characteristics of the PI-1 Membrane[a]

PI Conc. (wt %)	NMP/DCM (wt ratio)	PWF (L/m² h)	Solute Retention (%)			
			10,000	20,000	35,000	50,000
	77/0	180	62	87	92	> 99
23	72/5	142	65	94	97	> 99
	67/10	86	83	96	> 97	> 99
	62/15[b]	—	—	—	—	—

[a] Casting and evaluation conditions were the same as in the preceding case. Membrane was prepared from the newly direct method.
[b] PI was insoluble in NMP/DCM (62/15 w/w) solvent system.

Table VII   Permeation Characteristics of Dried PI-1 Membrane Treated With Different Drying Agents[a]

Drying Agent	PWF (L/m² h)	Solute Retention (%)			
		10,000	20,000	35,000	50,000
Wet[b]	180	62	87	92	> 99
Glycerin	140	65	90	96	> 99
Water	78	78	95	99	> 99
Mixture[c]	100	63	90	97	> 99

[a] Casting and evaluation conditions were the same as in the preceding case. The dried membranes were doped initially in agent for 24 h and then dried at room temperature for seven days.
[b] Untreated membrane.
[c] The mixture was consisted of water and glycerin (1 : 1 w/w).

Table VIII   Permeation Characteristics of Various PI Membranes[a]

PI No.	PI Conc. (wt %)[b]	PVP Contents (% w/w PI)	PWF (L/m² h)	Solute Retention (%)			
				10,000	20,000	35,000	50,000
PI-2	18	0	274	< 10	42	63	> 99
		10	300	< 10	29	50	> 99
		20	350	< 10	< 10	37	93
		30	440	< 10	< 10	25	90
PI-3	18	0	113	30	82	92	> 99
		10	130	< 10	51	85	> 99
		20	173	< 10	42	80	> 97
		30	200	< 10	29	80	> 97
PI-4	25	0	140	30	61	86	> 99
		10	161	< 10	44	84	> 99
		20	200	< 10	35	68	> 99
		30	240	< 10	30	57	> 99
PI-5	20	0	66	50	66	85	> 99
		20	100	30	42	63	> 99
PI-6	20	0	50	63	64	95	> 99
		20	82	32	40	90	> 99

[a] Casting and evaluation conditions were the same as in the preceding case.
[b] There was maximum concentration in NMP to form the membrane.

membrane with increased thickness;[9,13] thus, the diffusion and permeability constant might be inversely proportional to the membrane thickness. The SR of all the membranes showed up to about 90% against PEG 20,000. From the result, it could be probably explained that the SR was determined mainly by the dense upper layer of membrane. Therefore, the variation of SR with different thickness was relatively small compared to that of flux. The durability of the membrane with 150 μm thickness was significantly dwindled with operation period. From the result, it showed very poor performance.

In order to investigate the role of additive in membrane performance, PVP (MW: 10,000) as an additive was added to the casting solution. The membranes containing 10, 20, 30, and 50% (w/w) PVP in polymer were prepared and evaluated. PVP is a quite hydrophilic polymer and has been used as a preferable additive to improve polymeric membranes.[14-16] Table V shows the results on the influence of PVP in the casting solution. From the result, the PWF was gradually increased while the SR was decreased with increasing PVP contents. It means that the porosity of membrane might be increased by increasing of PVP contents. While the nascent membrane was immersed in the water bath and/or rinsed with water, the PVP in the membrane might be dissolved and flowed out of the membrane. Hence, the membrane was induced to form larger pores within the dense upper layer as well as porous sublayer. The SR was significantly diminished by the enlarged pores in the dense layer.

One of the main variables in the solvent evaporation process has been the choice of the solvent/cosolvent system.[13,17] For obtaining the membrane
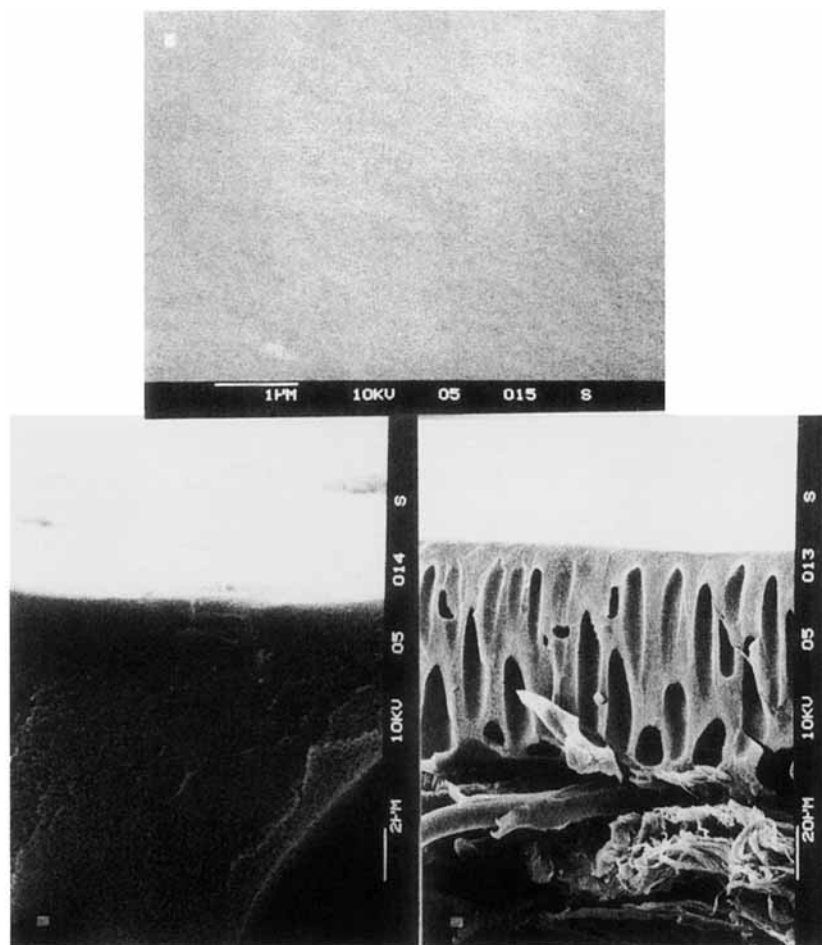

(a)

Figure 4 SEM of the top surface and cross section of (a) wet, (b) dried, and (c) immersed in 3N-NaOH PI-1 membrane.

with high SR, it is necessary that the gradient of solvent concentration in the dense layer should become smaller than that in the porous sublayer. This is achieved by the vigorous solvent evaporation from the surface of the nascent membrane during the solvent evaporation period. In this investigation, the mixed solvent system composed of high boiling solvent NMP and more volatile DCM as a cosolvent was used for increasing the amount of evaporating solvent during evaporation period. The performance of membrane as a function of DCM portion in the mixed solvent system is summarized in Table VI. The PWF decreased dramatically while the SR was only slightly increased by increasing the DCM portion. The polymer density of the upper layer in the nascent membrane might be gradually increased by increasing the portion of volatile DCM. Thus, the upper layer of membrane was more densely formed. In the case of 62/15 ratio (w/w) NMP/DCM, the

homogeneous casting solution could not be prepared because of the phase separation of the polymer solution. From the results, the performance of membrane could be controlled by introduction of solvent/cosolvent systems.

A great part of the membranes have been carried out in wet state and also stored in that state because the performance of polymeric membranes might be changed in the dried state and could not regain its initial properties.[13] Thus, the storage and treatment have been very difficult. In order to investigate the dried conditions in the performance of membrane, the prepared wet membranes were initially immersed into different agents and then dried at room temperature for seven days. Table VII shows the variation of membrane performance according to differently dried agents. The PWF of dried membranes was decreased some, while the SR was slightly increased compared to wet membrane. The decreasing
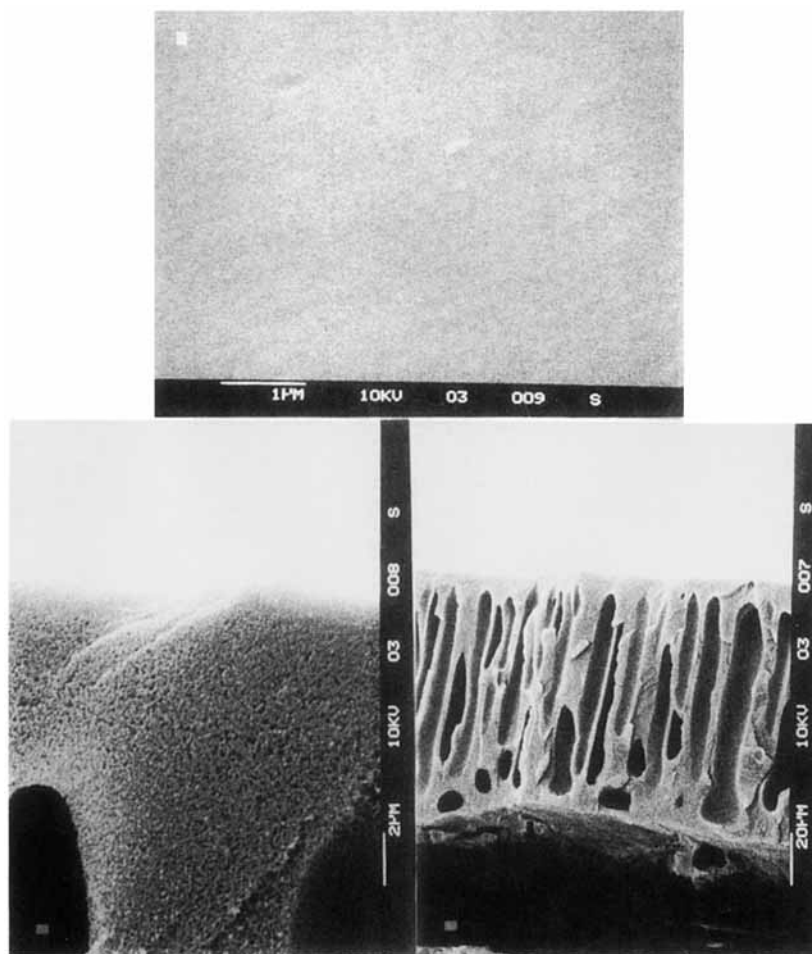
**(b)**

Figure 4   (*Continued from the previous page*)

trend of the PWF of the dried membrane treated with 1/1 (w/w) glycerin/water mixed agent was higher than that with glycerin. On the other hand, the SR values of both the membranes were about the same. The reasons for this result were unclear, but the result might be related to the change of the intermolecular force. While the membrane was dried, they were subject to shrinkage and warp because cohesion force between polymer chains might be changed. From the results, the performance of the dried PI membranes was slightly changed, although the intermolecular forces was considerably changed by eliminating solvent, water, and/or immersed reagents.

The PWF and the SR of various PI membranes are summarized in Table VIII. All the polymer concentrations were at maximum solubility in NMP to form the membrane. As shown in the table, the PWF of all the membranes increased, while the SR de-

creased by increasing PVP contents. Those phenomena were similar to the PI-1 membrane.

In order to elucidate structure of the PI membranes, the cross section and surface of the membranes were observed with a SEM. Figure 4 represents the SEM photographs of PI-1 membrane obtained from the wet, dried state, and immersed 3N-NaOH aqueous solution. In all the photographs, there were gradually dense structures progressing from the bottom to the top part of membranes. Through these structural observations, they consisted of a very dense top layer with extremely thin thickness and a supported porous sublayer; in other words, the prepared membranes were highly asymmetric structure.

The chemical stability of polymeric membrane has been limited with respect to pH and various organic liquids. Thus, PI derivatives have become of increasing interest as membrane materials because of their outstanding thermal and chemical stability in com-
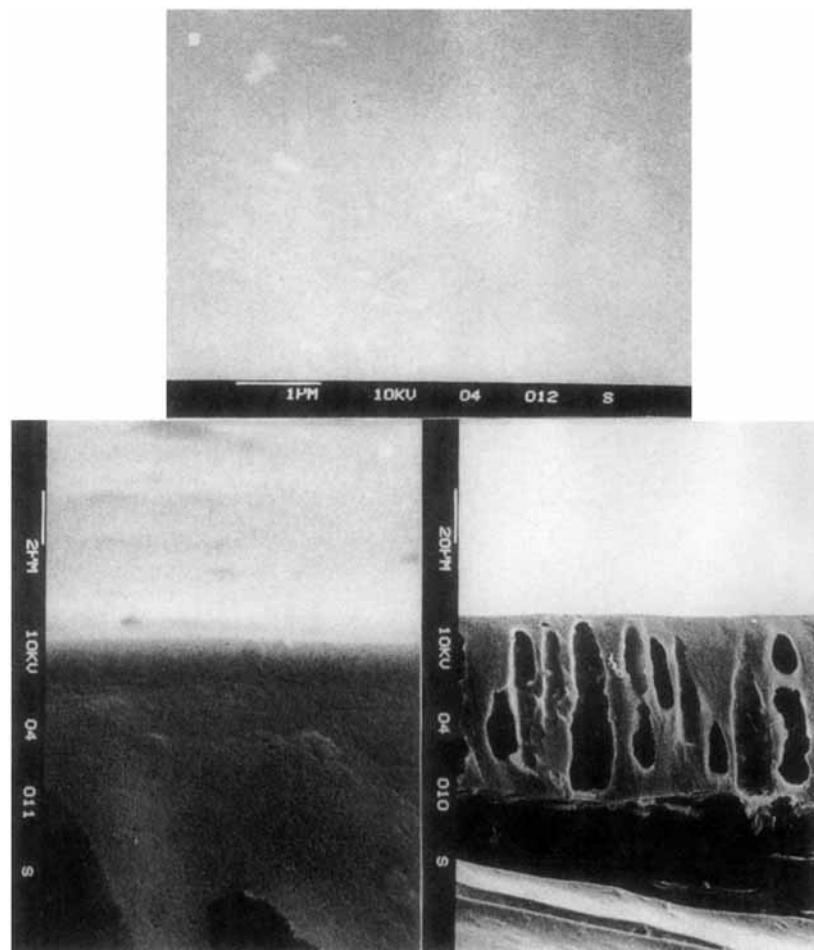
(c)

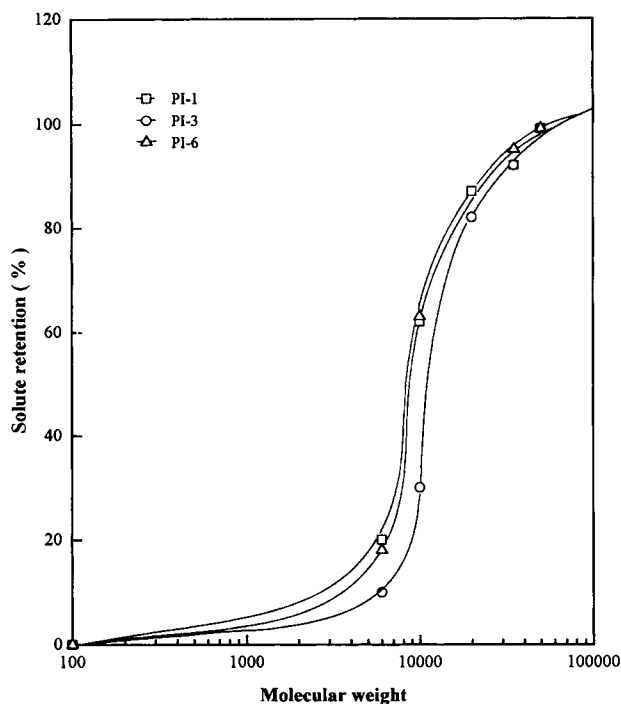**Figure 4** (Continued from the previous page)

parison to other polymers. Table IX represents the chemical stability of PI-1 membranes. They were immersed in various organic liquids. After seven days, they were washed several times with pure water, and then the permeation characteristics was observed by the UF apparatus. As shown in the Table IX, the PWF and SR values were not changed drastically among the common organic liquids; on the other hand, the PI membrane was only unstable in some aprotic polar solvents such as NMP, DMAc, DMF, and so on. Although the membrane immersed in 3N-NaOH was swelled somewhat in the porous sublayer (Fig. 4), the permeation was nearly unchanged. It means that the PI membranes showed highly chemical stability. The number of applications can be expected to increase.

The concept of molecular weight cut-off has been used frequently to indicate the performance of a given membrane.[9,13] Cut-off is defined as that molecular weight which is 90% rejected by the membrane. In order to determine the molecular weight cut-off characteristics of PI membranes, the SR of the membranes against the PEG aqueous solution in the range of molecular weight from 6000–50,000 was calculated. Figure 5 represents the molecular weight cutoff of PI membranes. Those values of PI membranes were about 20,000.

Figure 5 The molecular weight cutoffs of the PI membranes.

Table IX Evaluation of Organic Solvent Resistance on the Permeation Characteristics of PI-1 Membrane[a]

Solvent	PWF (L/m² h)	Solute Retention (%) MW 20,000	Remarks
Water	180	87	
Acetic acid	183	88	
Acetone	180	87	
Benzene	180	87	
Chloroform	176	87	
m-Cresol	—	—	dissolve
3N-HCl	182	88	
Hexane	180	91	
3N-NaOH	186	83	
Pyridine	500	20	swell
DMAc	—	—	dissolve
NMP	—	—	dissolve
DMSO	—	—	dissolve
DMF	—	—	dissolve

[a] The membrane were immersed in each solvent at room temperature for seven days before testing.

CONCLUSION

The newly asymmetric PI membranes prepared from the conventional method and the newly developed one. Since the PI derivatives as membrane material have a good solubility in some aprotic polar solvents without much sacrifice in thermal and chemical stability, the dope solution could be prepared directly from the PI solution via the one-step polymerization from monomers in the new method.

The permeation characteristics of PI membranes could be controlled by the several factors, such as polymer concentration, casting thickness, the amount of additive, solvent/cosolvent system, etc. Specifically, the permeation of dried PI membranes was changed slightly compared to the corresponding wet one, and all the membranes showed good chemical stability. Therefore, both wet and dried membranes were able to be used for organic solvent-resistance membranes. The PI membranes are considered quite a breakthrough for the application because of the following characteristics: (1) good flux and SR; (2) wide temperature limit and fairly good organic solvent resistance because the PI is an outstanding thermal and chemical stable polymer; (3) easy membrane formation because of improved PI solubility in some polar solvents and the control

of the influenced parameters; and (4) easy to control and transport because of the nearly unchanged characteristics of a wet membrane and the corresponding dried one.

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