Preparation of Polyimide Composite Membrane by Chemical Vapor Deposition and Polymerization Technique (CVDP)

H. YANAGISHITA,* T. NAKANE, H. NOZOYE, and H. YOSHITOME

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

SYNOPSIS

A dry process of chemical vapor deposition and polymerization (CVDP) was employed to prepare a polyimide composite membrane for water–ethanol separation, using an apparatus newly developed for this investigation. The characteristics of the apparatus were studied by depositing pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (P,P'-oxydianiline, ODA) in a vacuum of 10^{-6} Torr. Deposited layers were converted to a thin polyimide film by heating at 200°C for 3 h in a vacuum. The composite membranes were prepared by forming a polyimide layer of 0.2 μm thickness on the surface of asymmetric supporting membranes made by the phase-inversion process. The polyimide composite membrane prepared under the best conditions exhibited a separation factor α (H_2O/EtOH) of over 140 for 95 vol % aqueous ethanol solution with flux of 0.1 kg/m^2 h at 25°C in pervaporation mode. Also, it was demonstrated that this new technique of chemical vapor deposition and polymerization (CVDP) was very useful for the preparation of a solvent-resistant composite membrane in a completely dry process. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

In recent years, the chemical vapor deposition and polymerization (CVDP) technique has been investigated for making a thin solventless polymer film in a completely dry process.[1,2] It was reported that thin films made from the solvent-resistant polymers such as polyamide and polyimide could also be formed by this new technique.[3] However, most of these investigations have been performed for the purpose of physical applications such as that of a protect film for a liquid-crystal display device. There has been no work aimed at applying this technique to other chemical purposes such as the preparation of separation membranes and other functional materials.

In the field of membrane technology, the phase-inversion process has been generally used for the preparation of asymmetric membranes from various polymers. There are, however, some restrictions to this process, i.e., a polymer used as a membrane material must be soluble in a certain solvent for the preparation of a casting solution, and both membrane morphology and the fine structure of its surface (active layer) must be simultaneously controlled at the gelation step.

Therefore, a composite membrane is more desirable than an asymmetric membrane in high membrane performance. A composite membrane has a thin layer coated onto the surface of a porous supporting membrane by *in situ* polymerization and other methods. But up to now, a heat- and solvent-resistant composite membrane for reverse osmosis, pervaporation, and gas separation has never been developed.

In this investigation, the preparation of a polyimide composite membrane by the CVDP technique was studied using the apparatus developed for this work, and the applicability of this new dry process was confirmed experimentally.

---

in high vacuum
$<10^{-6}$

Polymerization by heating

Active layer

Composite membrane
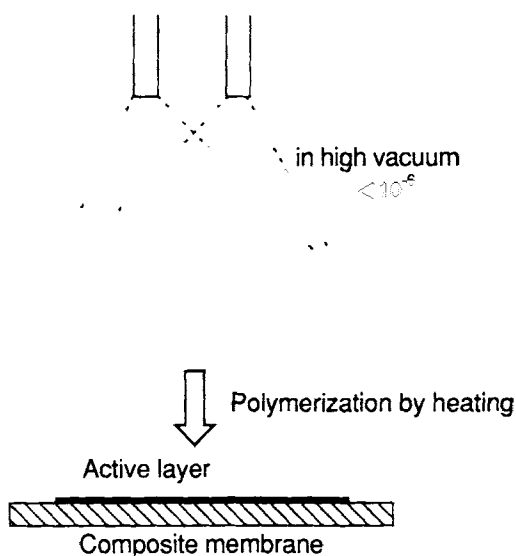
2. PROCESS DESCRIPTION

The preparation process of making the polyimide composite membrane by the CVDP technique is schematically shown in Figure 1. Two kinds of monomers are effused as molecular beams from source ovens in a vacuum (10^{-6} Torr) and deposited

on the surface of an asymmetric polyimide membrane. The deposited monomers are converted to a polyimide layer by heating. It is assumed that the vacuum of 10^{-6} Torr serves to form the collision-free molecular beams and to prevent the influence of trace amounts of water on the monomer reaction.

a. CVDP Apparatus

A newly developed apparatus for this investigation was used to prepare a polyimide composite membrane of 8 cm diameter by the CVDP process. The schematic of our apparatus is shown in Figure 2. It consists of the three parts: the vacuum chamber made of stainless steel (SUS-304) with the internal volume of 75,000 cm^3 (40 cm ϕ × 60 cm), the evacuation systems set up with the combination of a turbo molecular pump (1.5 m^3/min) and a rotary vacuum pump, and the devices for the effusion of monomers. For viewing the internal appearance, a glass window of 30 cm diameter was put in the front of the main chamber, and one of 10 cm diameter, to the front side of the quick entry chamber. The attainable vacuum level of the apparatus was designed to be at 10^{-8} Torr.

Each monomer was individually but simultaneously effused from its own source device and deposited on the substrate set on its holder upside
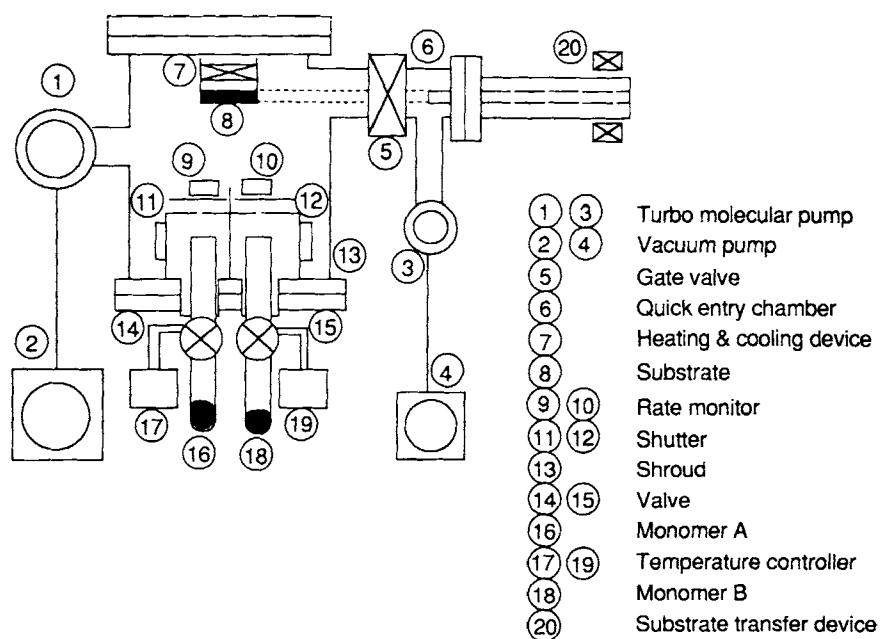

① ③	Turbo molecular pump
② ④	Vacuum pump
⑤	Gate valve
⑥	Quick entry chamber
⑦	Heating & cooling device
⑧	Substrate
⑨ ⑩	Rate monitor
⑪ ⑫	Shutter
⑬	Shroud
⑭ ⑮	Valve
⑯	Monomer A
⑰ ⑲	Temperature controller
⑱	Monomer B
⑳	Substrate transfer device

Figure 2 Membrane preparation apparatus of the CVDP technique.

down. The effusion rates of the two monomers were controlled by the temperature of the source devices, valves [(14) and (15)] and shutters [(11) and (12)]. The amounts of the deposited monomer were measured by an Inficon crystal oscillator [(9) or (10)].

The passages through which the monomers were effused from their source devices were maintained at temperatures sufficient to prevent the condensation of these monomers.

b. Materials

Reagent-grade pyromellitic dianhydride (PMDA) and 4,4-diaminodiphenyl ether (oxydianiline, ODA) were used as monomers without additional purification, as purchased from the Tokyo Kasei kougyo Co. Figure 3 shows the reaction scheme of these monomers.

An asymmetric polyimide membrane was used as a supporting membrane after curing at adequate temperature (300°C), which was prepared by the phase-inversion process in our laboratory using the aromatic polyimide (PI-2080) available from the Dow Chemical Co.[4] The membrane used for aqueous solutions had a molecular weight cutoff performance of about 10,000.
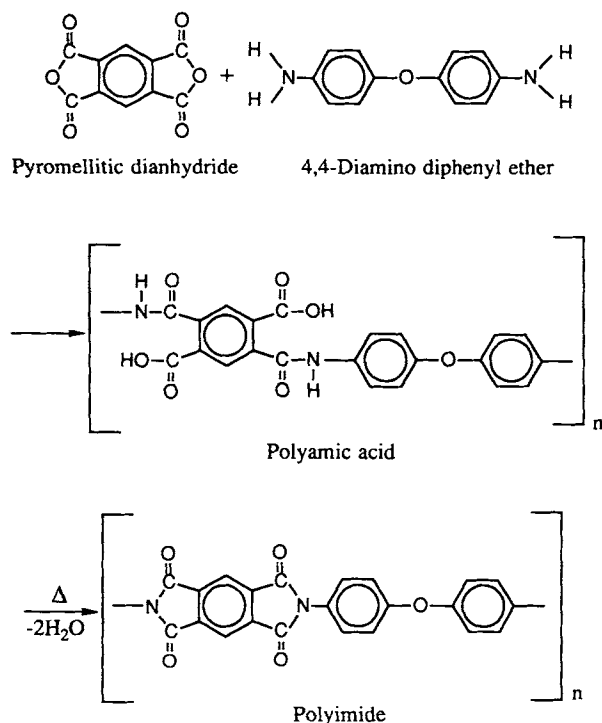
Pyromellitic dianhydride   4,4-Diamino diphenyl ether

Polyamic acid

Δ
$-2H_2O$

Polyimide

Figure 3   Polymerization scheme of pyromelitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA).
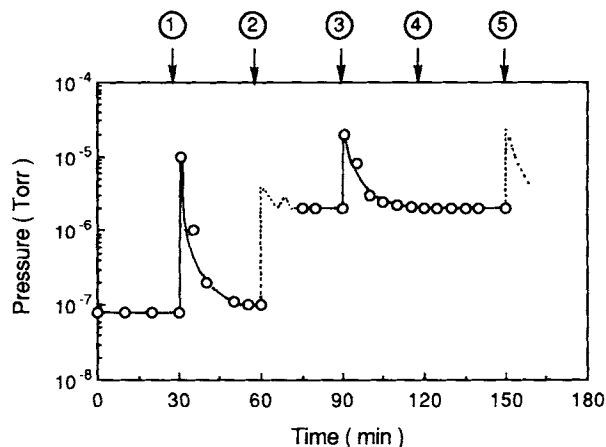
Figure 4   Deposition procedure of CVDP apparatus: ① glass plate input; ② monomer valve open; ③ glass plate output, polyimide membrane input; ④ deposition start; ⑤ deposition end.

c. Deposition Procedure

The deposition and polymerization of the monomers were performed in the following manner using the apparatus mentioned above:

The apparatus was first operated to maintain the vacuum at below 10^{-6} Torr. The deposition sources were heated by ovens at 300°C for PMDA (mp, 286°C) and 200°C for ODA (mp, 190°C), respectively.

1. A glass plate substrate was put in the quick entry chamber and set on the holder (8) in the main chamber using the substrate transfer device.
2. After the system had returned to a steady state, the effusion of each monomer was started and controlled as required.
3. Both shutters (11) and (12) were closed and the glass plate substrate was taken out of the apparatus. The polyimide supporting membrane was put in the main chamber and set on the substrate holder (8).
4. After the system returned to the steady state again, the shutters were open and the deposition of the monomers was performed for a suitable period.
5. The shutters were closed again, and then the supporting membrane was taken out of the apparatus.

It was then cured in another vacuum oven. This procedure is schematically shown in Figure 4. Preparation of the composite membranes at the same conditions was easily repeatable.

d. Characterization Methods

The amount of deposited monomers were measured by chemical analysis, i.e., the monomers deposited on the glass plate were dissolved in methanol and their concentrations were determined by octadecyl silica (ODS) liquid chromatograph.

The extent of the reaction of the deposited monomers was monitored by Fourier transform infrared (IR) spectroscopy using an attenuated total reflection attachment (ATR–FTIR).

The polyimide composite membranes prepared by the CVDP technique were verified by separation performance of the water–ethanol system in the pervaporation mode. The pervaporation experiments were performed at 25°C and at under 1 Torr of permeate side pressure. The concentration of a feed or permeate solution was determined by ODS liquid chromatograph or GPC (gel permeation chromatograph).

Figure 6 Relation between amount of deposited monomers and time: (○) ODA.

4. RESULTS AND DISCUSSION

a. Characterization of the CVDP Apparatus

The newly developed CVDP apparatus was first examined for its attainability of a vacuum and the controllability of monomer deposition. The use of the Viton O-ring in the door greatly increased the ease of opening and closing the main chamber. The evacuation performance without monomer effusion is shown in Figure 5. A vacuum of below 10^{-6} Torr could be easily obtained within 10 h after the begin-
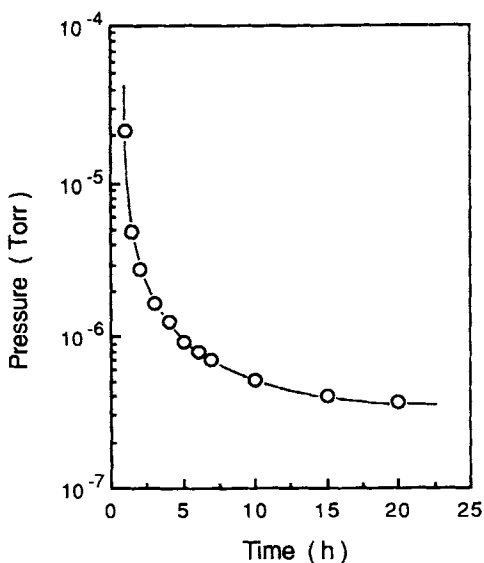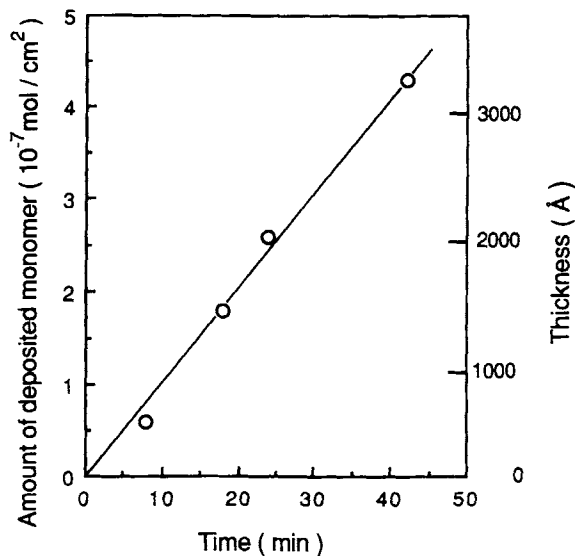
ning of the evacuating operation. Three days were required to attain the higher vacuum level of below 10^{-7} Torr without any baking treatment.

The controllability of the monomer deposition was studied by the direct deposition onto a glass plate at a constant temperature. Figure 6 shows that the amount of the deposited ODA increased in proportion to the operation time and the deposition rate was constant under the applied conditions. As shown in Figure 7, the thickness indicated by the deposition
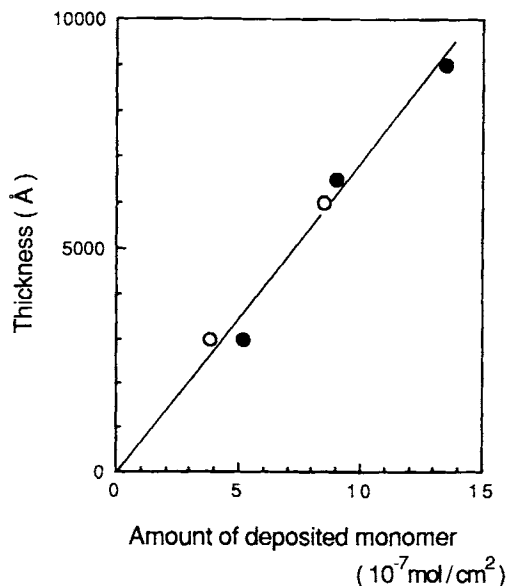

Figure 5 Evacuating performance of CVDP apparatus.

Figure 7 Relation between amount of deposited monomers and thickness in deposition rate monitors: (○) PDMA; (●) ODA.
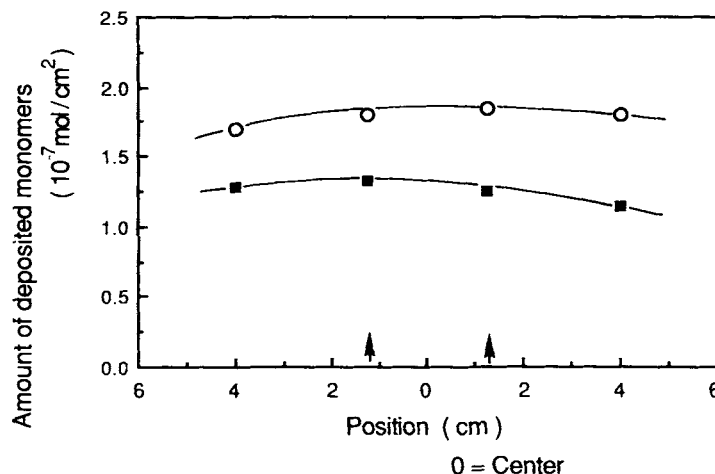
Figure 8 Distribution of deposited monomers: (○) ODA; (■) PDMA.

rate monitors [Inficon crystal oscillators (9) and (10)] was in direct proportion to the amount of the deposited monomers. From these procedures, it was found that the deposition rates of each monomer could be controlled by the valves attached to the molecular beam source devices using the deposition rate monitors and that the deposition rates were considerably larger in value (about 30–90 Å/min) compared to those obtained by conventional plasma polymerization techniques.[5]

The thickness uniformity was confirmed by examining the distribution of the deposited monomers on the glass plate. As the results show in Figure 8, the monomers were almost uniformly deposited within the designed area of 4 cm radius for the preparation of polyimide composite membrane.

b. Formation of Polyimide Thin film

For the chemical characterization of the codeposited layers, both monomers of PMDA and ODA were simultaneously deposited on an aluminum plate about 2000 Å in thickness at the stoichiometric ratio of 1 : 1, and the infrared spectra of the codeposited layer was measured by ATR-FTIR. The results obtained are shown in Figure 9. The absorption bands of polyamic acid at 1,600–1,700 cm^{-1} were observed in the layer just after the deposition. These bands, however, disappeared with heating at 300°C, and the peak of the C — N stretching vibration due to the imide bond appeared at 1380 and 1750 cm^{-1}. This means that the first step reaction shown in Figure 3 takes place immediately after the deposition in vacuum without any catalyst and the deposited monomers are converted to polyamic acid. Therefore, the membrane with the codeposited layer could be taken out of the CVDP apparatus and moved to an ordinary vacuum for the conversion of the deposited layer to polyimide by heating (the second step reaction in Fig. 3).

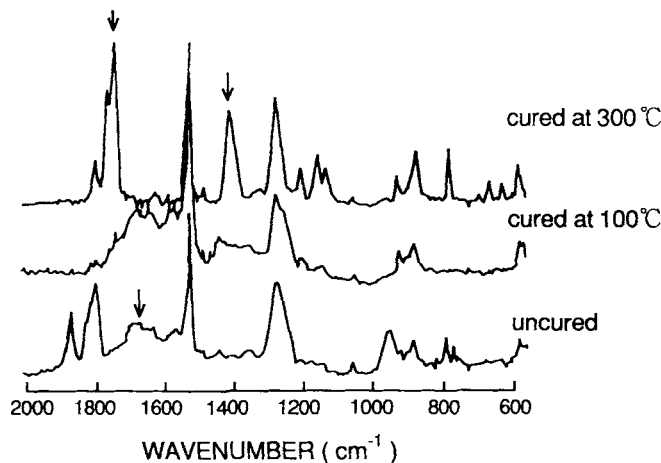The effects of heating temperature and period on

Figure 9 FTIR spectra of deposited layers.

this dehydration reaction were also studied by FTIR measurement. They are shown in Figure 10, where the extent of the imidization reaction is indicated as the ratio of the peak intensities ($C-N$ stretching vibration of imide bond at 1380 $cm^{-1}/C-O-C$ stretching vibration at 1480 cm^{-1}). It is seen that the imidization reaction proceeded with the heating temperature and period and was completed by heating at 300°C for over 1 h. It was, however, considered that the deposited layer could also be converted enough to the polyimide thin film by heating at 200°C for 3 h. We, therefore, determined the curing condition for the preparation of polyimide composite membranes as heating at 200°C for 3 h in an ordinary vacuum oven. This means that the supporting membranes require heat resistance above 200°C.

c. Preparation of Polyimide Composite Membrane

In this investigation, the asymmetric polyimide membrane was used as the supporting membrane, which was prepared by the phase-inversion process from the casting solution composed of 25 wt % polyimide and 75 wt % N,N-dimethylformamide (DMF). The strength and solvent resistance of asymmetric polyimide membranes increase with the annealing temperature. The effect of the heat treatment on the asymmetric polyimide membrane was examined by the pervaporation method using a 95 vol % aqueous ethanol solution at 25°C. The results are summarized in Table I. The membrane cured at
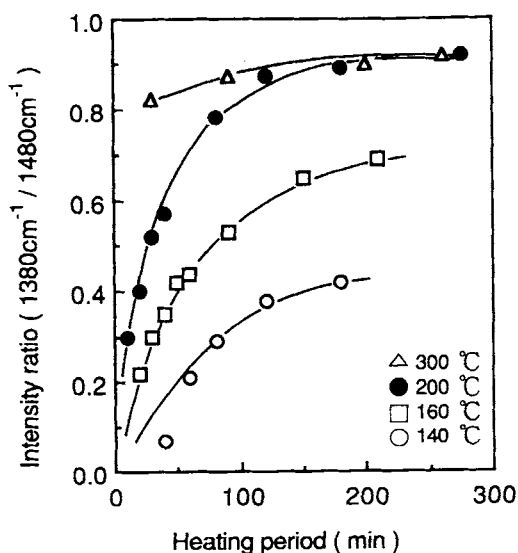
Table I Effect of Heat Treatment on Asymmetric Polyimide Membrane (Supporting Membrane)

Condition	Flux (kg/m² h)	$\alpha_{EtOH}^{H_2O}$ (—)
No treatment	7.30	1
In carboxylic ester (270°C, 3 h)	0.67	4
In vacuum (10^{-2} Torr)		
(300°C, 6 h)	0.22	60
(350°C, 6 h)	0.02	3

Measurement conditions: feed solution, 95 vol % EtOH; temperature, 25°C; secondary pressure, < 2 Torr.

300°C for 6 h in a vacuum of below 10^{-1} Torr showed water permeability. The membrane cured at 350°C showed lower performance in both flux and separation factor. We believe that this was due to the glass transition temperature of this polyimide being about 315–320°C.[6] The membrane cured at 270°C in dicarboxylic ether also did not show good performance. From these results, it was confirmed that the asymmetric aromatic polyimide membrane could be used as a substrate of the composite membrane if it is annealed at 300°C for 6 h in a vacuum of below 10^{-1} Torr.

Table II shows the performance of the composite membranes prepared by the CVDP technique under different conditions, where the thickness of the deposited monomers are equal (0.2 μm). The difference of the separation factor α in these three membranes was thought to be caused by two factors: It was thought that the polyimide thickness of membrane (b) was about 0.2 μm and that of membrane (a) or (c) was about 0.1 μm, because PMDA and ODA reacts at the stoichiometric ratio of 1 : 1, as shown in Figure 3. The formation of the active layer of membrane (a) or (c) is incomplete, and some im-

Figure 10 Effects of heating temperature and period on condensation reaction of deposited layers.

Table II Separation Performance of Polyimide Composite Membrane

Deposited Monomer Ratio PMDA : ODA	Flux (kg/m² h)	$\alpha_{EtOH}^{H_2O}$ (—)
Supporting membrane	0.22	60
(a) 3 : 1	0.06	113
(b) 1 : 1	0.10	144
(c) 1 : 3	0.05	45

Measurement conditions: feed solution, 95 vol % EtOH; temperature, 25°C; secondary pressure, < 1 Torr. PMDA: pyromellitic dianhydride. ODA: 4,4-diaminodiphenyl ether (P,P'-oxydianiline).

perfection remained in the active layer. Furthermore, in the case of membrane (c), the surface layer of the asymmetric supporting membrane is also attacked by the excess of ODA in the heating process.

The polyimide composite membrane prepared at the best conditions of a monomer ratio (1 : 1) exhibited the separation factor α of over 140 for 95 vol % aqueous ethanol solution with the flux of 0.1 kg/m² h. It was considered that the CVDP technique was very applicable for the preparation of a solvent-resistant composite membrane.

Finally, the cross section of the polyimide composite membrane prepared at the best conditions of a monomer ratio (1 : 1) was observed by scanning electron microscopy, and the results are shown in Figure 11. From these photographs, the skin layer made by this CVDP process was observed on the surface of an asymmetric polyimide membrane.

5. CONCLUSION

The preparation of polyimide composite membranes by the chemical vapor deposition and polymerization (CVDP) technique were investigated to confirm the applicability of this new dry process using the ap-

paratus developed for this work, and the following results were obtained:

Concerning the CVDP technique, it was found that the deposition rates of each monomer were all completely controllable, and each monomer could be deposited uniformly within the designed area of 8 cm diameter for the preparation of composite membranes. Relatively high deposition rates of 30–90 Å/min were obtained compared with the conventional plasm polymerization technique. The mixed deposition layer of pyromelitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA) could be easily converted to the polyimide layer by heating at 200°C for over 3 h in an ordinary vacuum.

Concerning the preparation of polyimide composite membranes, it was found that the asymmetric polyimide membrane made by the phase-inversion process could be used as the substrate of the composite membrane after heating at 300°C for 6 h in a vacuum of below 10^{-1} Torr, and it was confirmed that the polyimide composite membrane could be prepared by forming the ultrathin polyimide layer (about 0.2 μm thickness) on the surface of the asymmetric polyimide membrane by use of this CVDP technique. The membrane that exhibited the best performance had a separation factor α (H₂O/EtOH) of over 140 for 95 vol % aqueous ethanol
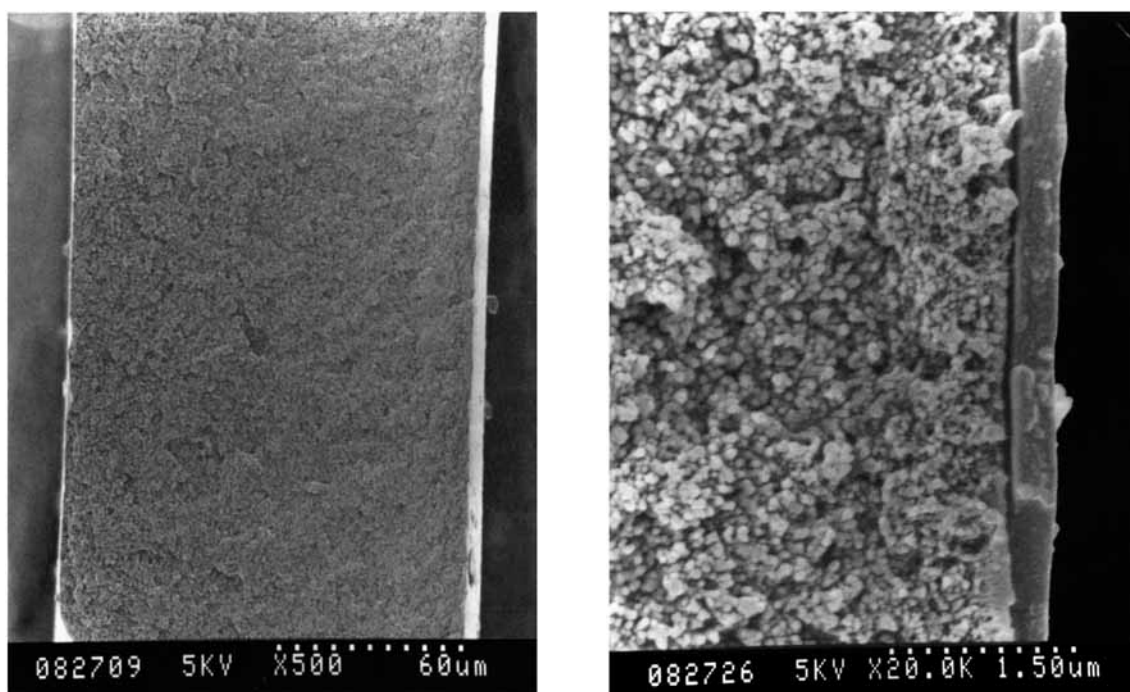

Figure 11 Cross section of polyimide composite membrane observed by scanning electron microscopy (SEM). Deposition thickness: PMDA 0.1 μm; ODA 0.1 μm.

solution with flux of 0.1 kg/m^2 h at 25°C in the pervaporation mode.

From these results, it was concluded that the CVDP technique was very effective for the preparation of heat- and solvent-resistant composite membranes.

REFERENCES

1. J. R. Salem, F. O. Sequedal, J. Duran, and W. Y. Lee, *J. Vac. Sci. Technol.*, **A4**, 369 (1986).

2. M. Grunze and R. N. Lamb, *J. Vac. Sci. Technol.*, **A4**, 1685 (1987).
3. Y. Takahashi, T. Nakane, and M. Yoshitome, *J. Vac. Sci. Technol.*, **A5**, 2253 (1986).
4. H. Yanagishita, M. Iijima, K. Inagawa, and A. Itoh, in *The 1987 International Congress on Membranes and Membrane Processes (ICOM'87)*, 1987, p. 267.
5. R. d'Agostino, *Plasma Deposition, Treatment, and Etching of Polymers*, Academic Press, New York, 1990.
6. M. N. Sarbolouki, *J. Appl. Poly. Sci.*, **29**, 743 (1984).