Gas Separation of Asymmetric 6FDA Polyimide Membrane with Oriented Surface Skin Layer

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ABSTRACT: A novel asymmetric polyimide membrane with an oriented surface skin layer was prepared by a dry−wet phase inversion process at different shear stresses. The surface morphology and the structure of the membranes were characterized by scanning electron microscopy and atomic force microscopy. Molecular orientation in the membranes was investigated using polarized ATR-FTIR spectroscopy. We found that the shear rate controlled by a doctor blade affects the thickness and morphology of the surface skin layer and the structure of the membrane. The gas permeances of a novel asymmetric polyimide membrane with an oriented surface skin layer were measured using a high-vacuum apparatus with a Baratron absolute pressure gauge at 76 cmHg. Both the gas permeance and selectivity of the asymmetric polyimide membranes increased with an increase in the shear rate. This may be due to the fact that the molecular orientation induced in the membrane influenced the diffusion of gas molecules through the oriented skin layer and that the gas diffusivity selectivity increased with decreasing skin layer thickness. Finally, the gas selectivity in the asymmetric polyimide membrane was enhanced. Discussions were carried out on the correlation between the shear rate and the membrane formation or the gas permeability.

Introduction

The gas separation process by polymer membranes has received much attention during the past several decades. Recently, much attention has been paid to the separation of greenhouse gases from industrial waste gases using polymer membranes. Membrane separation is considered one of the most practical approaches to the separation of CO_2, an important greenhouse gas, from industrial gases. An additional advantage is that membrane systems provide better energy efficiency than conventional separation methods. An important objective for a gas separation membrane is the development of new polymer membranes combining high gas permeability and selectivity, which becomes a subject of strong research interest.[1−3]

We have reported gas transport through a novel asymmetric polyimide membrane with a thin, defect-free skin layer prepared by a dry−wet phase inversion process, which is formed using three components (a ternary system), polymer/solvent/nonsolvent.[4−6] The phase inversion process involves the phase separation of a polymer solution in polymer-rich and -lean phases, which can be achieved by an immersion−precipitation technique. The calculated apparent skin layer thickness of the asymmetric polyimide membrane was approximately 10 nm, and the membrane showed a 5.3 (O_2/N_2) selectivity at an O_2 permeance of 7.9×10^{-4} [cm^3 (STP)/(cm^2 s cmHg)]. We succeeded in preparing a novel asymmetric polyimide membrane with an ultrathin and defect-free skin layer, which realized significantly high gas permeance. Additionally, to enhance the gas selectivity of the membrane, it is required to modify the thin, defect-free skin layer which dominates the gas transport properties.

It has been recognized that molecular orientation will affect the gas selectivity of a membrane.[7−9] Shilton et al. have reported that shear and elongation during spinning have been shown to affect the gas permeation performance of a polysulfone hollow fiber membrane.[10−12] The coated fiber membrane showed high gas selectivity, while the membrane without a coating with silicone exhibited relatively low selectivity, suggesting the presence of pores. They concluded that a highly ordered active layer on the membrane was formed by shear stress and that the layer led to a high gas selectivity. To prepare a membrane having both high gas permeance and selectivity, we have fabricated a novel asymmetric polyimide membrane with a defect-free skin surface orientated by shear stress without a coating process.

Molecular orientation in the membrane can be directly measured using spectroscopic techniques. Polarized ATR-FTIR spectroscopy is used to characterize the surface molecular orientation of the asymmetric polyimide membrane. Spectroscopy is a suitable technique for the membrane because it can detect information from only a thin surface with a depth of less than 150 nm.[13−16]

In this study, the gas permeances of a novel asymmetric polyimide membrane with an oriented surface skin layer have been measured using a high-vacuum apparatus with a Baratron absolute pressure gauge at 76 cmHg. Molecular orientation in the membranes was investigated using polarized ATR-FTIR spectroscopy. We focused on the effect of shear stress, which leads to molecular orientation, on the gas permeance and selectivity of the asymmetric polyimide membranes.

Experimental Section

Materials. 2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from Clariant Co. (Shi-

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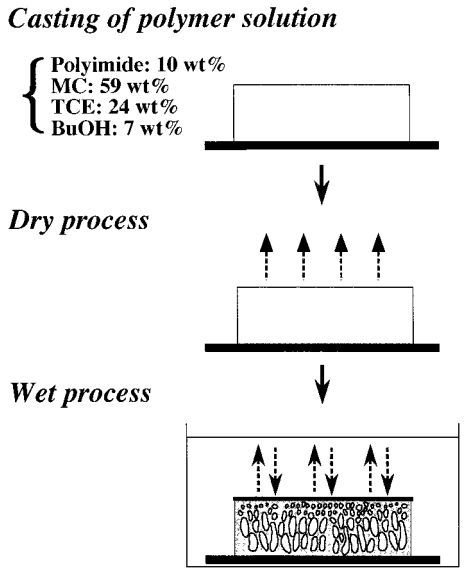

Figure 1. Schematic representation of dry−wet phase inversion process.

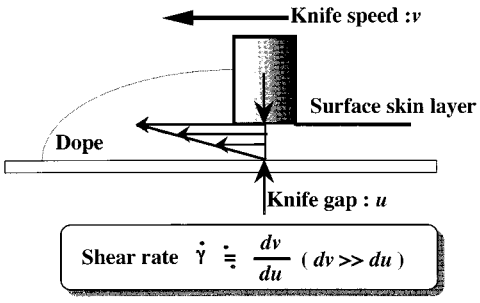

Figure 2. Schematic description of the asymmetric membranes made by various shear conditions.

Table 1. Shear Conditions of Asymmetric Polyimide Membranes Made by Dry−Wet Phase Inversion Process

membrane	knife gap [μm]	knife speed [cm/s]	shear rate [s^{-1}]
PI-100	300	3	100
PI-500	300	10	500
PI-750	300	20	750
PI-1000	300	30	1000

zuoka, Japan) and purified by sublimation prior to use. 2,2′-Bis(4-aminophenyl)hexafluoropropane (6FAP) was purchased from Central Glass Co. (Saitama, Japan) and recrystallized twice in methylene chloride solution prior to use.

Fluorinated polyimide, 6FDA-6FAP, was synthesized from the chemical imidization of the poly(amic acid) precursors as reported in the literature.[17,18] The synthesized 6FDA-6FAP had a M_w of 4.8×10^5 with a polydispersity index of 2.6.

Preparation of Asymmetric 6FDA Polyimide Membranes. Asymmetric 6FDA polyimide membranes which have a defect-free surface skin layer supported by a porous substructure were prepared by a dry/wet phase inversion process (Figure 1) as previously reported in the literature.[4,5] 6FDA polyimide solutions composed using three solvents—methylene chloride (MC), 1,1,2-trichloroethane (TCE), and 1-butanol—were prepared. After being filtered and degassed, the polyimide solutions were cast on a glass plate by a doctor blade at a controlled shear rate (Figure 2) and were air-dried for 15 s containing the shear process at room temperature. The operation of a doctor blade was carefully carried out by a hand. The shear conditions used in this study are listed in Table 1. The times for the shear process depended on the shear rate and changed from 1 to 3 s. The membrane areas stretched out by a doctor blade were from 10×10 to 10×30 cm^2. After evaporation, the membranes were coagulated in methanol, washed for 12 h, air-dried for 24 h at room temperature, and finally dried in a vacuum oven at 150 °C for 15 h to remove all of the residual solvents.

Surface Characterization of Asymmetric 6FDA Polyimide Membranes. The cross sections of the asymmetric polyimide membranes were observed with a scanning electron microscope (SEM, JXP-6100P, JEOL, Tokyo, Japan).

Surface morphology of the asymmetric polyimide membranes was visualized by an atomic force microscope (AFM, SPI3700, Seiko, Tokyo, Japan) in air at room temperature. Standard Si_3N_4 cantilevers (SN-AF01, Seiko), with a spring constant of 0.021 N/m, were used and operated in the noncontact mode. The surface was continuously imaged in the feedback mode with a scan area of 500×500 nm and at a constant scan speed of 2 Hz. The surface roughness parameter of the membranes was presented by R_a, which is an arithmetic mean of departure of the roughness profile from the mean line.

Polarized ATR-FTIR spectra of asymmetric polyimide membranes were measured on a Bio-Rad model FTS-60A FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector and an ATR accessory. The ATR accessory is composed of a square Ge crystal and a rotatable sample holder. Sixty-four scans of 2 cm^{-1} resolution were averaged to achieve a sufficient signal-to-noise ratio.

Gas Permeation Measurements. The purities of the carbon dioxide, oxygen, and nitrogen used in this study were 99.999%, and that of methane was 99.9%. These gases were used without further purification.

Asymmetric 6FDA-6FAP membranes were mounted on a permeation cell with a 1.0 cm^2 surface area. Gas permeances were measured with a high-vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan). The pressure on the upstream and the downstream sides was detected using a Baratron absolute pressure gauge. The gas permeation measurements of at least five membranes fabricated under the same preparation conditions were carried out at 35 °C and 76 cmHg, and their data showed good reproducibility. Additionally, gas permeability measurements were carried out over the temperature range 15−45 °C. The apparent skin layer thickness of the asymmetric polyimide membranes was calculated from

$$L = P/Q \tag{1}$$

where L [cm] is the apparent skin layer thickness, P [cm^3 (STP)cm/(cm^2 s cmHg)] is the gas permeability coefficient measured from the dense polyimide flat membrane, and Q [cm^3 (STP)/(cm^2 s cmHg)] is the gas permeance of the asymmetric polyimide membranes. L was determined from the oxygen permeability coefficient.

Results and Discussion

Characteristics of Asymmetric Membranes. Figure 3 shows the results of SEM observation of the asymmetric polyimide membranes, PI-100, PI-500, PI-750, and PI-1000. The preparation of asymmetric membranes cast by a doctor blade was carefully carried out at a controlled shear rate. PI-100, PI-500, PI-750, and PI-1000 were prepared at a shear rate of 100, 500, 750, and 1000 s^{-1}, respectively. All the structures consisted of a skin layer and a porous substructure, and the cross section of the PI-500, PI-750, and PI-1000 indicated a thin skin layer and a spongelike structure characterized by the presence of finger voids. In contrast, the membrane of PI-100 showed a spongelike structure. The SEM results gave us important information about the formation process of the membranes prepared at different shear rates.

It is well-known that, in a phase separation process, liquid−liquid demixing and polymer−liquid demixing in a polymer/solvent/nonsolvent system play very important roles in determining the membrane structures. We have reported that the liquid−liquid exchange rate

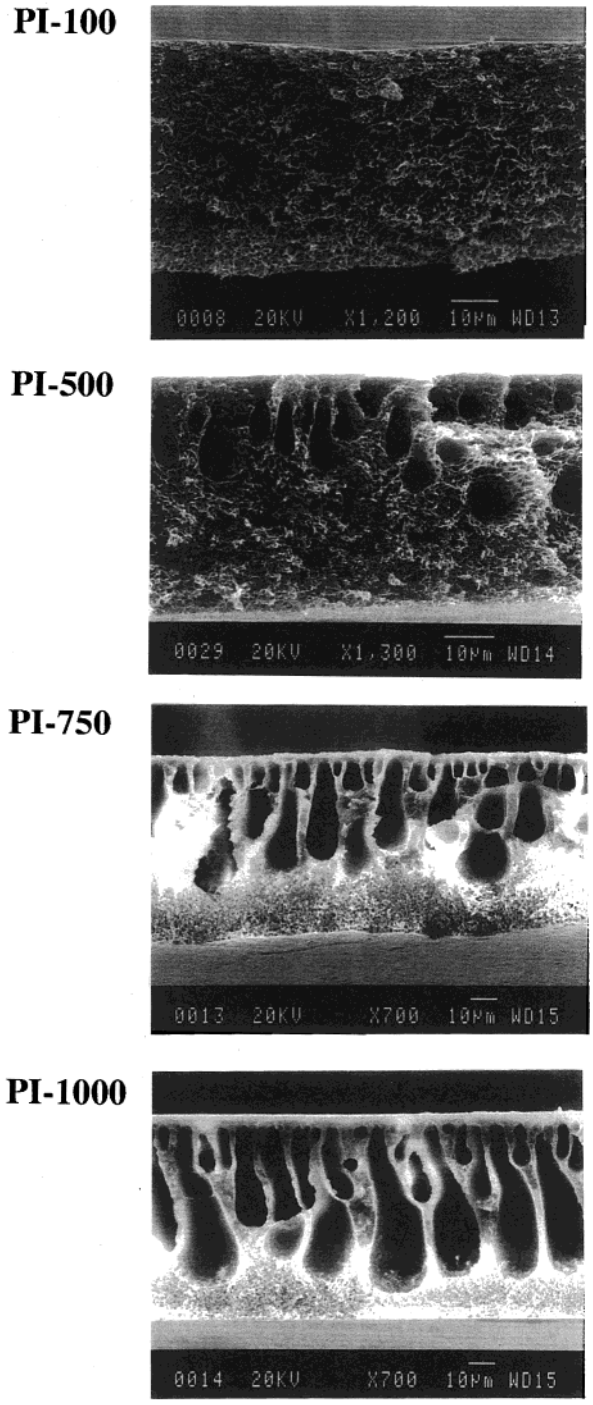

Figure 3. SEM photographs of cross section of the asymmetric polyimide membranes.

between the solvent and the nonsolvent has a great influence on the skin layer thickness and the membrane structure. Asymmetric membranes formed by instantaneous demixing had an ultrathin top skin layer supported by a finger-type structure, and the membranes formed by delayed demixing had a dense skin layer supported by a sponge-type structure. We believe that, at higher shear, instantaneous demixing occurred between the solvent and nonsolvent so that the membrane consisted of a skin layer and a finger-type structure. In contrast, at lower shear, delayed demixing occurred so that the membrane consisted of a dense skin layer and a spongy-type structure. The phase separation for hollow fiber formation has usually carried out under tension or stress. It has been reported that such stresses create extra phase instability, facilitate phase separation, and induce orientation.[19] Therefore, the phase separation behavior observed in the asymmetric membrane prepared under stress may be similar to that reported in the hollow fiber. However, the future research will need to elucidate a phase separation process determining the asymmetric membrane structure.

Liquid−liquid demixing in a phase separation process also plays very important roles in determining the surface morphology of the membrane. Figure 4 shows the AFM image of the top surface of an asymmetric polyimide membrane prepared at different shear rates in a three-dimensional form over an area of 500 × 500 nm. The differences in the morphology are evaluated by the roughness parameters such as R_a, which is an arithmetic mean of the departures of the roughness profile from the mean line. The R_a values of asymmetric membranes prepared from the shear rate of 100, 500, 750, and 1000 s^{-1} were 10.0, 11.8, 12.6, and 14.6 Å, respectively, and were larger than that of determined for a dense membrane (1.8 Å). One interesting aspect at the surfaces is that there are good correlations between R_a and shear rate. In a previous paper, we reported that a faster exchange rate between the solvent and nonsolvent in a phase separation process led to a larger surface roughness and a thinner skin layer thickness of the asymmetric membrane.[4] The AFM results obtained in this study indicate that shear stress also influences the exchange rate between solvent and nonsolvent and that the asymmetric membrane prepared at higher shear, which leads to a faster exchange rate, had a greater roughness and a thinner skin layer.

It is clear from Figure 4 that there was a decrease in the average size of nodules when the shear rate increased. Matsuura reported that discrete nodules are defined by the regularly occurring and distinct depressions shown by the AFM image, while merged nodules are defined by a smooth appearance on the membrane surface.[20−22] Nodules observed on PI-100, PI-500, and PI-750 surfaces had diameters of 500−1000 Å, indicating nodule aggregates. On the other hand, the nodule size on the PI-1000 surface was approximately 200 Å, indicating macromolecular aggregates. We believe that the higher shear causes an enhancement of molecular orientation of the polyimide in a phase separation process and that the orientated polyimide aggregates form discrete nodules. In contrast, the degree of orientation formed by lower shear was low so that the nodules were aggregated.

Molecular orientation in the asymmetric membranes prepared at different shear rates was measured using polarized ATR-FTIR spectroscopy. Figure 5 shows the IR spectra of PI, PI-100, and PI-1000. The bold line represents the spectra measured with the polarization parallel to the casting direction, and the normal line represents the spectra with the polarization perpendicular. There was no difference in absorbance between the parallel and perpendicular polarization measured for PI and PI-100. However, the difference observed in PI-1000 was larger, indicating that the asymmetric polyimide membrane with a perpendicularly oriented skin was prepared. We found that the shear rate induced by a doctor blade affects the polyimide structure of the surface skin layer on the membrane.

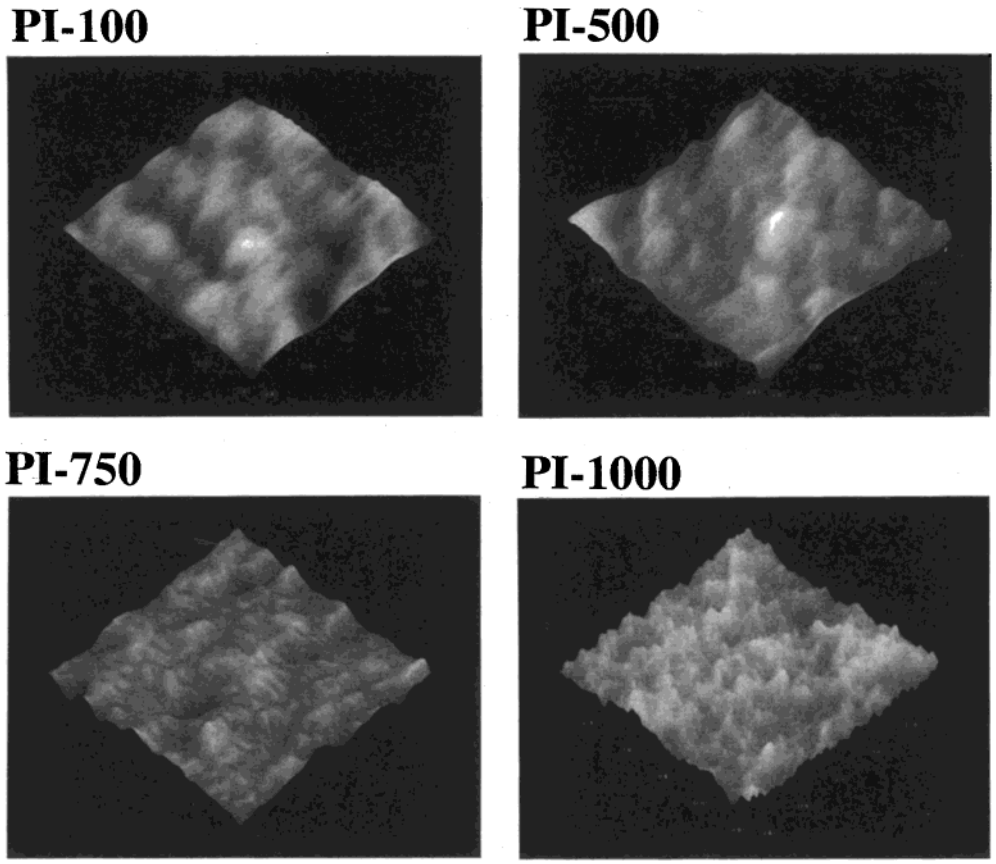

Figure 4. Three-dimensional AFM images of top surface of the asymmetric polyimide membranes.

Gas Transport Properties of Asymmetric Membranes. The results of gas permeance and selectivity of the dense and asymmetric polyimide membranes for CO_2, O_2, N_2, and CH_4 at 35 °C and 76 cmHg are shown in Table 2. The gas selectivities of the asymmetric membranes, PI-100, PI-500, PI-750, and PI-1000, were greater than those of a dense membrane, which indicates that the transport of the asymmetric membrane is predominantly carried out by a solution-diffusion mechanism and that the surface skin layer is essentially defect-free. Additionally, all the asymmetric membranes used in this study were not plastisized by CO_2. We have already found that an asymmetric polyimide membrane with an ultrathin skin layer of 50 nm thickness is not plastisized by 380 cmHg of CO_2.[23]

It should be noted that both the gas permeance and selectivity of the asymmetric membranes increases with an increase in the shear rate. Generally, the more common polymer membranes show a trend of decreasing polymer selectivity with increasing permeability. However, the gas selectivity of the asymmetric polyimide membranes prepared under shear stress depended on the skin layer thickness and increased with decreasing thickness. We have already reported the effect of the skin layer thickness of the asymmetric membrane on gas selectivity.[5] We propose that the asymmetric polyimide membrane with a thinner surface skin layer forms a more packed structure and that the packed structure in the surface skin layer that is formed by the intermolecular interactions provides a high size and shape discrimination between the gas molecules.

To elucidate the gas transport properties of the asymmetric membrane prepared at different shear rates, permeability measurements for CO_2, O_2, N_2, and CH_4 were carried out over the temperature range 15−45 °C. Activation energies for the permeance (ΔE_p) of the asymmetric polyimide membranes for PI-100, PI-500, PI-750, and PI-1000 are shown in Figure 6. Interestingly, the ΔE_p clearly was enhanced with decreasing skin layer thickness and was larger than that determined in the dense membrane. These results suggest that some contributions affect the growth of potential barriers for gas permeability, as reflected in the increase in the ΔE_p on the surface of a thinner polyimide membrane, so that the gas selectivity increases for the asymmetric membranes with a thin surface skin layer. Obviously, from Figure 5, an increase in shear rate has a significant influence on the orientation of the polyimide. We believe that the oriented structure in the surface skin layer becomes a barrier to gas permeability and provides a high size and shape discrimination between the gas molecules.

According to the solution-diffusion mechanism, ΔE_p can be expressed as a function of the heat of sorption (ΔH_s) and the diffusion activation energy (ΔE_d) as follows:

$$\Delta E_p = \Delta H_s + \Delta E_d$$

The influence of ΔH_s, ΔE_d, and ΔE_p on the gas permeability in 6FDA polyimides was already investigated by Kim or Xu, and they suggested that ΔE_d rather than ΔH_s is a more predominant factor for ΔE_p.[24,25] Unfortunately, in the asymmetric polyimide membrane, the time lag before establishing steady-state straight lines of gas permeability was so short that we could not calculate the diffusion and solubility coefficients using the time lag. However, we consider that ΔE_p determined

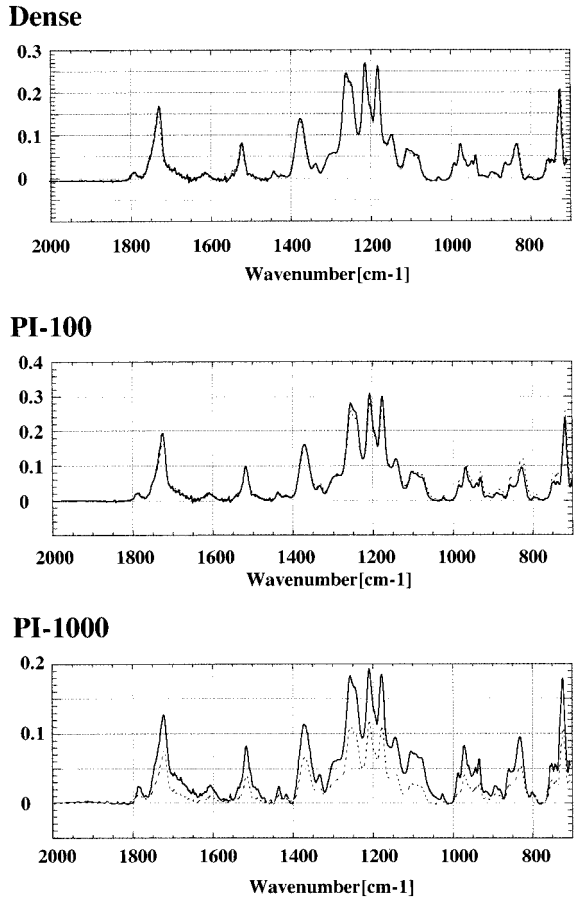

Figure 5. Polarized ATR−FTIR spectra of asymmetric polyimide membranes: (—) parallel to spinning direction; (- - -) perpendicular to spinning direction.

Table 2. Gas Permeances and Selectivities of Asymmetric Polyimide Flat Membranes Made by Various Shear Rates[a]

membrane	QO_2	QCO_2	QO_2/QN_2	QCO_2/QCH_4	L
dense	0.21	1.0	4.7	33	38600
PI-100	6.3 ± 0.4	30 ± 1	4.7 ± 0.03	34 ± 0.9	1290 ± 45
PI-500	12 ± 0.5	59 ± 2	4.8 ± 0.02	37 ± 0.8	670 ± 37
PI-750	23 ± 1	120 ± 4	4.9 ± 0.04	38 ± 1.0	340 ± 11
PI-1000	66 ± 2	340 ± 9	5.1 ± 0.06	41 ± 1.2	120 ± 5

[a] Temperature = 35 °C; gas pressure = 76 cmHg; $Q = 10^{-6}$ [cm^3 (STP)/(cm^2 s cmHg)]; L = apparent skin layer thickness [nm].

in the membrane also strongly depends on ΔE_d. That is, the molecular orientation in the membrane influenced on the diffusion of gas molecules through the oriented skin layer so that the diffusivity selectivity of DO_2/DN_2 and DCO_2/DCH_4 increased with decreasing skin layer thickness. Finally, the QO_2/QN_2 and QCO_2/QCH_4 of the membrane with the oriented surface skin layer was enhanced with an increase in DO_2/DN_2 and DCO_2/DCH_4.

Our greatest interest was the free volume and free volume distribution formed in the oriented surface skin layer, which dominate the gas transport properties. A gas separation membrane having a large free volume and a narrow free volume distribution can indicate both enhanced gas permeability and selectivity. Although we could not clarify the correlation between the molecular orientation and the free volume or free volume distribution, we believe that the molecular orientation in the development of a novel gas separation membrane is one of the important membrane fabrication technologies

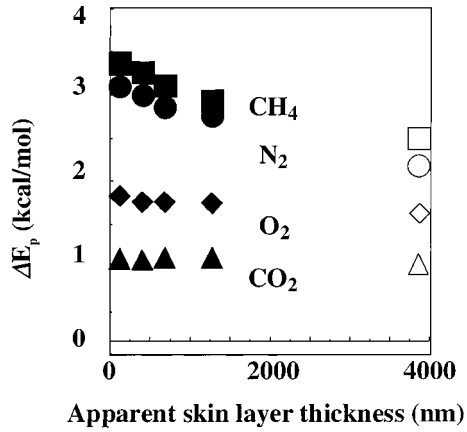

Figure 6. Effect of apparent thickness of skin layer on the ΔE_p for the asymmetric polyimide membranes at 76 cmHg.

controlling the free volume and free volume distribution. In further research, we will try to fabricate a novel membrane with a more highly oriented surface.

Conclusions

A novel asymmetric polyimide membrane with an oriented surface skin layer was prepared by a dry−wet phase inversion process at the different shear stresses. We found that the shear rate was one of the very important factors in determining the surface morphology and the structure of the membrane. The surface of the membrane prepared at a high shear rate was covered by nodules, while that of the membrane at a low shear rate was covered by nodular aggregates. The cross section of the membranes prepared at a high shear rate indicated a thin skin layer and a spongelike structure characterized by the presence of finger voids. In contrast, the membrane at a low shear rate showed a spongelike structure. These results are due to the fact that the shear has a great influence on the exchange rate between solvent and nonsolvent in a phase separation process.

Molecular orientation in the asymmetric polyimide membranes was investigated using polarized ATR−FTIR spectroscopy. There was no difference in absorbance between the parallel and perpendicular polarization measured for the dense membrane and the asymmetric membrane prepared at a low shear rate. On the other hand, the difference observed in the membrane prepared at high shear rate was larger, indicating that a membrane with a perpendicular oriented skin was prepared. We found that the shear rate induced by a doctor blade affects the polyimide structure of the surface skin layer in the membrane.

The gas permeances of a novel asymmetric polyimide membrane with the oriented surface skin layer were measured using a high-vacuum apparatus with a Baratron absolute pressure gauge at 76 cmHg. Interestingly, both the gas permeance and selectivity of the asymmetric membranes increases with an increase in the shear rate. We suggest the following aspects of the gas selectivity for the asymmetric polyimide membrane with the oriented surface skin layer. The molecular orientation induced in the membrane mainly influenced the diffusion of gas molecules through the oriented skin layer, and consequently, the gas diffusivity selectivity increased with decreasing skin layer thickness and the gas selectivity was enhanced.

In the gas separation membrane, it is desirable to fabricate a novel polymer membrane with both high gas permeability and selectivity. One approach is to prepare a membrane with a large free volume and a narrow free volume distribution. In this study, we demonstrated that the gas permeance as well as the gas selectivity increased with an increase in shear rate. These results may indicate that shear stress significantly influences the free volume distribution in the oriented surface skin layer. In further research, we will elucidate the correlation between the molecular orientation and the free volume or free volume distribution in the oriented membrane.

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