

Structure and Gas Permeation Properties of Asymmetric Polyimide Membranes Made by Dry–Wet Phase Inversion: Influence of the Polyimide Molecular Weight

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ABSTRACT: In this article, we report the influence of the polyimide molecular weight (1.2×10^5 , 2.6×10^5 , and 4.1×10^5) on the structure and the gas permeation properties of asymmetric polyimide membranes made by the dry–wet phase-inversion process. The apparent skin layer thickness of the asymmetric membrane increased with increasing molecular weight, and the thicknesses of the membranes prepared from the three polyimides with a casting polymer solution containing 8.0 wt % butanol were 132, 350, and 739 nm, respectively. That is, the gas perme-

ance in the asymmetric membranes increased with decreasing molecular weight. In contrast, the gas selectivity of the asymmetric membranes did not depend on the skin layer thickness. The solvent evaporation in the dry phase-inversion process and the nonsolvent diffusion in the dry process were important factors that determined the formation of the asymmetric membrane. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 105–112, 2010

Key words: gas permeation; membranes; polyimides

INTRODUCTION

Polymer membranes are considered an effective technology for the separation of gaseous mixtures because of their high separation efficiency, low operating costs, and simple operation. The development of an asymmetric membrane consisting of a thin, defect-free skin layer supported by a porous substructure has attracted much attention for gas separation.^{1–5} The gas permeation properties of these asymmetric membranes are primarily determined by the properties of the skin layer. The skin layer should be defect free and as thin as possible to achieve the maximum gas permeability and selectivity. However, it is extremely difficult to make an asymmetric membrane with a thin, defect-free skin layer because pores or defects on the order of 5–10 Å are easily formed on the surface of the asymmetric membranes when they are made.

To prepare a thin, defect-free asymmetric membrane, a dry–wet inversion process was developed by Pinnau and coworkers^{6–8} They succeeded in preparing asymmetric polysulfone membranes with a defect-free skin layer of less than 100 nm. We also

prepared an asymmetric polyimide membrane with a thin, defect-free skin layer using the dry–wet phase-inversion process; this membrane was formed with three components (a ternary system), that is, a polymer, solvent, and nonsolvent.^{9–13} The asymmetric membranes were cast from a polyimide, dichloromethane (DCM), 1,1,2-trichloroethane (TCE), and butanol (BuOH). The phase-inversion process involves the phase separation of a polymer solution into polymer-rich and polymer-lean phases; this can be achieved by an immersion–precipitation technique. We succeeded in preparing the asymmetric polyimide membrane with an ultrathin (ca. 10 nm) and defect-free skin layer using the phase-separation technique.

In a previous study, we reported that the molecular weight of the polyimide influenced the gas permeation stability of an asymmetric polyimide membrane with an ultrathin and defect-free skin layer made by the dry–wet inversion process.¹⁴ For example, in the case of the CO₂ permeation through the membrane, CO₂ plasticization of the membrane prepared with the high-molecular-weight polyimide was significantly suppressed. In addition, we demonstrated that the molecular weight of the polyimide influenced the skin layer structure of the asymmetric polyimide membrane prepared under shear stress.¹⁵ The skin layer of the membrane prepared from the low-molecular-weight polyimide indicated a high gas selectivity because the molecular orientation in the skin layer of the asymmetric membrane was easily formed. That is, these findings indicate that the

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molecular weight plays an important role in the formation of the skin layer. We postulated that the molecular weight of the polyimide is an important factor determining the structure and the gas permeation properties of asymmetric membranes made by the dry-wet inversion process. However, few studies regarding the influence of the molecular weight on the properties of the membranes have been reported.

In this article, we report the influence of the molecular weight of the polyimide on the structure and the gas permeation properties of asymmetric polyimide membranes made by the dry-wet phase-inversion process. The membrane-forming solvents were DCM, TCE, and BuOH. The gas permeances of the asymmetric membranes prepared from the different molecular weights were measured with a high-vacuum apparatus equipped with a Baratron absolute pressure gauge at 76 cmHg and 35°C.

EXPERIMENTAL

Materials

2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from Central Glass Co. (Saitama, Japan) and was purified by sublimation before use. The diamine monomer was 2,2'-bis(4-aminophenyl)hexafluoropropane (6FAP), which was also purchased from the Central Glass, and was recrystallized twice in ethanol before use.

Synthesis and characterization of 6FDA-6FAP

The polyimide, 6FDA-6FAP, was synthesized by the chemical imidization of poly(amic acid) precursors as reported in the literature.^{9,16} We prepared 6FDA-6FAP with three monomer concentration ratios [6FDA (mol):6FAP (mol) = 0.104 : 0.104, 0.039 : 0.039, and 0.049 : 0.048]. The poly(amic acid)s were prepared by solution condensation at room temperature and at 14 wt % solid content in dimethylacetamide under a nitrogen atmosphere. After they were stirred for 12 h, the poly(amic acid) precursors were converted into the corresponding polyimides at room temperature by chemical imidization with 5 equiv of acetic anhydride and triethylamine. After a reaction of 48 h, the polyimides were precipi-

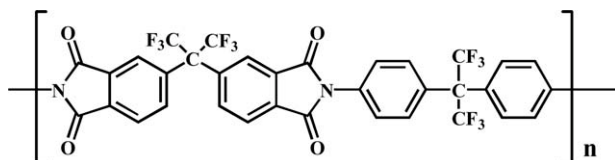


Figure 1 Chemical structure of 6FDA-6FAP.

TABLE I
Composition of the Casting Polyimide Solutions

Polyimide concentration (wt %)	DCM concentration (wt %)	TCE concentration (wt %)	BuOH concentration (wt %)
16	59	18	7.0
16	59	17.5	7.5
16	59	17	8.0

tated by methanol (MeOH), recovered, and filtered. Subsequently, the polyimides were washed with MeOH several times and dried in a vacuum oven at 150°C for 24 h. The structure of 6FDA-6FAP is shown in Figure 1.

The weight-average molecular weight (M_w) and number-average molecular weight of 6FDA-6FAP were determined by gel permeation chromatography (830-RI monitor detector, Jasco, Tokyo, Japan) with tetrahydrofuran as the solvent. A flow rate of 1.0 mL/min was used, and the polyimide was dissolved in tetrahydrofuran at a concentration of 0.005 wt %. The molecular weights were estimated by the comparison of the retention times in a column (Shodex, KF-805L, Tokyo, Japan) to those of standard polystyrene.

Preparation of the asymmetric polyimide membranes

The asymmetric polyimide membranes were made with a dry-wet phase-inversion process. The casting polyimide solutions were made with polyimide, DCM, TCE, and BuOH, as shown in Table I. After they were filtered and degassed, the polyimide solutions were cast on a glass plate with a doctor blade and then air-dried for 30 s at room temperature. After evaporation, the membranes were coagulated in MeOH, 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.

Structure and surface characterization of the asymmetric membranes

The cross sections of the asymmetric polyimide membranes were observed by scanning electron microscopy (SEM; JXP-6100P, JEOL, Tokyo, Japan). The membranes were cryogenically fractured in liquid nitrogen and then coated with Pt/Pd.

The surface morphology of the asymmetric membranes was visualized by atomic force microscopy (AFM; SPI3700, Seiko, Tokyo, Japan) in air at room temperature.^{17,18} The cantilevers (Olympus SN-AF01), with a spring constant of 0.38 N/m, were microfabricated from silicon nitride. The surface was continuously imaged in the feedback mode with a scan area of 750 × 750 nm² and a constant scan

speed of 2 s^{-1} . The average arithmetic area surface roughness parameter (R_a) of the membranes was characterized.

Evaluation of the interaction parameters

The nonsolvent–polymer interaction parameter (χ_{13}) is expressed by the following simple equation:¹⁹

$$\chi_{13} = \{\ln(1 - \phi_p) + \phi_p\} / \phi_p^2 \quad (1)$$

where ϕ_p is the volume fraction of the polymer and can be obtained by a swelling experiment. Dried strips of the dense 6FDA–6FAP membranes were immersed in nonsolvents at 25°C .

The solvent–polymer interaction parameter (χ_{23}) was obtained with the following equations:^{20,21}

$$A_2 = \frac{16\pi N_0 [\eta]}{M\{9.3 \times 10^{24} + 4\pi N_0 c([\eta] - [\eta]_\theta)\}} \left\{ 1 - \frac{[\eta]_\theta}{[\eta]} \right\} \quad (2)$$

$$\chi_{23} = 1/2 - A_2 \rho_2^2 v_1 \quad (3)$$

where A_2 is the second virial coefficient, π is 3.14, N_0 is Avogadro's constant, c is the concentration (g/cm^3), $[\eta]$ is the intrinsic viscosity (cm^3/g) of the polymer in a given solvent, $[\eta]_\theta$ is its intrinsic viscosity under θ conditions, M is the average polymer molecular weight, ρ is the density of the polymer (g/cm^3), and v_1 is the molar volume of the solvent (cm^3/mol). The solution viscosities of the polyimide in DCM and TCE at 25°C were measured with an Ubbelohde viscometer (Toki Sangyo, Tokyo, Japan). The viscosities of the polyimides with molecular weights of 1.2×10^5 , 2.6×10^5 , and 4.1×10^5 in DCM were 25, 27, and $33 \text{ cm}^3/\text{g}$, respectively, and the viscosities in TCE were 62, 98, and $129 \text{ cm}^3/\text{g}$, respectively. The intrinsic viscosity was determined by the usual extrapolation to zero concentration.

Cloud measurement

The apparent cloud time was determined with polyimide solutions made from 16 wt % polyimide, 59 wt % DCM, 18 wt % TCE, and 7.0 wt % BuOH. After they were filtered and degassed, the polyimide

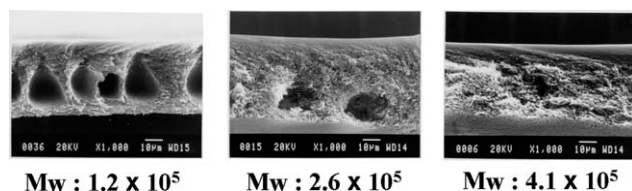


Figure 2 Micrographs of cross sections of the asymmetric polyimide membranes.

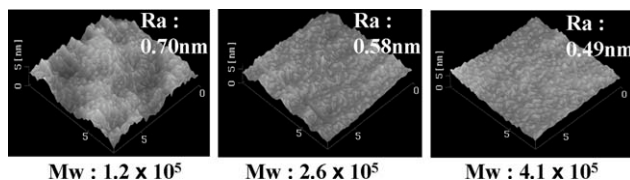


Figure 3 AFM images of the top surfaces of the asymmetric polyimide membranes.

solutions were cast on a glass plate with a doctor blade and then air-dried at room temperature. In addition, in the case of the wet process, the membrane was coagulated in MeOH. The cloud time was determined from the time when the initially clear membrane became visually cloudy during the dry–wet phase-inversion process.

Gas permeation measurements

The gas permeability coefficients of oxygen and nitrogen were measured with a high-vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan).^{9,10} The gas permeation measurements of the membranes were determined at 35°C and 76 cmHg. The apparent skin layer thickness of the asymmetric polyimide membranes was calculated as follows:

$$L = \frac{P}{Q} \quad (4)$$

where L is the apparent skin layer thickness (cm), which was determined from the oxygen permeability coefficient; P is the gas permeability coefficient [cm^3 (STP) $\text{cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$], which was measured from a dense polyimide flat membrane; and Q [cm^3 (STP)/($\text{cm}^2 \text{ sec cmHg}$)] is the gas permeance of the asymmetric polyimide membranes [cm^3 (STP) $\text{cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$].

RESULTS AND DISCUSSION

Structure of the asymmetric polyimide membranes

The molecular weight (M_w) and polydispersity index values of the synthesized 6FDA–6FAPs were 1.2×10^5 , 2.6×10^5 , and 4.1×10^5 and 2.3, 2.0, and 2.1, respectively. The molecular weights were estimated by a comparison of the retention times in a column to those of standard polystyrene.

Figure 2 shows the results of the SEM observations of the asymmetric polyimide membranes made from the dry–wet inversion process with different molecular weights. The skin layer thickness decreased in the following order: $4.1 \times 10^5 > 2.6 \times 10^5 > 1.2 \times 10^5$. The cross-sectional structure of all of the asymmetric membranes consisted of a thin skin layer and a porous substructure. The asymmetric membranes

TABLE II
Gas Permeation Properties of the Asymmetric Polyimide Membranes at 35°C and 760 mmHg ($M_w = 1.2 \times 10^5$)

BuOH concentration (wt %)	Q_{O_2} (GPU)	Q_{O_2}/Q_{N_2}	L (nm)
7.0	60	4.4	145
7.5	56	4.5	154
8.0	65	4.6	132

$$P_{O_2} = 8.7 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}; \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}.$$

prepared from molecular weights of 1.2×10^5 and 2.6×10^5 had spongelike structures characterized by the presence of finger voids, whereas the 4.1×10^5 membrane had only a spongelike structure.

Figure 3 shows AFM images of the top surface of the asymmetric polyimide membranes in a three-dimensional form over an area of $750 \times 750 \text{ nm}^2$. The asymmetric membranes were made by the dry-wet phase-inversion process with different molecular weights. The difference in the morphology was evaluated by R_a , which is the arithmetic mean of departure of the roughness profile from the mean line. The R_a values of the asymmetric membranes prepared from the 1.2×10^5 , 2.6×10^5 , and 4.1×10^5 polyimides were 0.70, 0.58, and 0.49 nm, respectively, and the roughness on the surface increased in the following order: $4.1 \times 10^5 < 2.6 \times 10^5 < 1.2 \times 10^5$. In a previous article, we reported that there was a good correlation between R_a and the skin layer thickness and that an asymmetric membrane with a larger parameter resulted in a thinner skin layer.¹⁰ Because the faster exchange rate between the solvent and nonsolvent on the surface of the asymmetric membrane was attributed to the larger roughness of the membrane, the results obtained in this study were similar to those already reported.

Gas permeation properties of the asymmetric polyimide membranes

The results of the gas permeance and selectivity values of the asymmetric polyimide membranes for O_2 and N_2 at 35°C and 76 cmHg are shown in

TABLE III
Gas Permeation Properties of the Asymmetric Polyimide Membranes at 35°C and 760 mmHg ($M_w = 2.6 \times 10^5$)

BuOH concentration (wt %)	Q_{O_2} (GPU)	Q_{O_2}/Q_{N_2}	L (nm)
7.0	32	4.5	404
7.5	33	4.4	387
8.0	37	4.6	350

$$P_{O_2} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}; \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}.$$

TABLE IV
Gas Permeation Properties of the Asymmetric Polyimide Membranes at 35°C and 760 mmHg ($M_w = 4.1 \times 10^5$)

BuOH concentration (wt %)	Q_{O_2} (GPU)	Q_{O_2}/Q_{N_2}	L (nm)
7.0	11	4.4	1200
7.5	18	4.1	754
8.0	18	4.5	739

$$P_{O_2} = 1.3 \times 10^{-9} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}; \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}.$$

Tables II–IV. The molecular weights of the polyimides were 1.2×10^5 , 2.6×10^5 , and 4.1×10^5 . The asymmetric membranes were made from three kinds of casting polymer solutions. The skin layer thickness of the asymmetric membrane was calculated from the oxygen permeability coefficient of the dense polyimide membrane. The O_2/N_2 selectivity of all of the asymmetric membranes were similar to that ($O_2/N_2 = 4.5$) of a dense membrane, which indicated that the permeation of the asymmetric membrane was predominantly determined by a solution–diffusion mechanism and that the surface skin layer was essentially defect free.

As is apparent from Tables II–IV, the gas permeance in the asymmetric polyimide membranes decreased with increasing molecular weight. The apparent skin layer thickness of the membrane was calculated from the oxygen permeability coefficient, and the calculated thicknesses of the asymmetric membranes prepared from the 1.2×10^5 , 2.6×10^5 , and 4.1×10^5 polyimides with the casting polymer solution containing 8.0 wt % BuOH were 132, 350, and 739 nm, respectively. The skin layer thickness decreased in the following order: $4.1 \times 10^5 > 2.6 \times 10^5 > 1.2 \times 10^5$. In particular, the skin layer thicknesses of the asymmetric membrane prepared from the 1.2×10^5 molecular weight polyimide indicated significantly low values compared with those determined in the membrane from the 4.1×10^5 polyimide.

In addition, the gas permeance or the apparent skin layer thickness of the asymmetric membranes strongly depended on the BuOH content in the casting polymer solution. We reported that the evaporation time during the dry process and BuOH content in the polymer solution are important factors in determining the thickness and structure of the skin layer.¹¹ In this study, the evaporation time was constant, and only the content of BuOH as a nonsolvent was changed. We considered that the high ratio of BuOH to solvent in the polymer solution immediately resulted in a phase separation and induced an instantaneous liquid–liquid exchange rate. That is, the rapid phase separation induced by BuOH appeared to generate the thinner skin layer.

TABLE V
Interaction Parameters of the Casting Solution and Polyimide at 25°C

M_w	χ_{13}		χ_{23}	
	MeOH	DCM	TCE	BuOH
1.2×10^5	1.13	0.41	0.28	0.98
2.6×10^5	1.13	0.47	0.35	1.00
4.1×10^5	1.13	0.48	0.43	1.02

In contrast, the gas selectivities of the asymmetric polyimide membranes were not dependent on the molecular weight of the polyimide and were constant. That is, although the molecular weight of the polyimide had a significant influence on the skin layer thickness, we considered that they did not influence the molecular orientation in the skin layer. In addition, the BuOH content in the casting polymer solution also hardly influenced the gas selectivity of the asymmetric membranes.

Skin layer formation of the asymmetric polyimide membranes

As mentioned previously, the molecular weight of the polyimide was one of the important factors determining the skin layer formation of the asymmetric polyimide membrane. To elucidate the influence of the molecular weight on the skin layer, we determined the binary interaction parameters for the polyimide/solvent/nonsolvent system and the apparent diffusion coefficients of the solvent in the casting polymer solution or nonsolvent as the coagulation medium.

The binary interaction parameters for the polyimide/solvent/nonsolvent system were investigated to examine the phase inversion occurring in the coagulation medium. The binary χ_{13} and χ_{23} values are summarized in Table V. The solvents in the casting polymer solution were DCM, TCE, and BuOH. The nonsolvent was MeOH as the coagulation medium. As is apparent from Table V, the χ_{13} values calculated from the polyimide and MeOH were almost constant; this indicated that the influence of χ_{13} on the skin layer formation of the asymmetric membrane was small. In contrast, the χ_{23} values increased with increasing molecular weight of the polyimide. In particular, the χ_{23} values for TCE dramatically changed and significantly increased with the molecular weight. We believe that χ_{23} as an interaction parameter of the solvent–polyimide had an influence on the phase inversion.

To elucidate the skin layer formation of the asymmetric membrane, we investigated the influence of a dry phase-inversion process on the formation. Table VI shows the apparent cloud time determined

from the time when the initially clear membrane visually became cloudy during the dry phase-inversion process. In general, there is a good correlation between the cloud time of the casting polymer solution and the phase separation of the polymer, and a short cloud time produces instantaneous phase separation in the polymer solution. As shown in Table VI, the time depended on the molecular weight of the polyimide and decreased with increasing molecular weight. In the dry process, the cloud time was closely related to the evaporation rate of the solvent in the polymer solution; therefore, the solvent prepared from the 4.1×10^5 molecular weight polyimide rapidly evaporated so that the instantaneous phase separation of the polymer was considered to be induced. As shown in Table V, although the χ_{13} values calculated from the polyimide and MeOH were almost constant, the χ_{23} values determined from the polyimide and solvent depended on the molecular weight; this suggested that the χ_{23} values might have influenced the evaporation of the solvent during the dry process. In general, a high χ_{23} indicates a low compatibility of the solvent and polymer, whereas a low χ_{23} indicates solvents and polymer with a high mutual affinity. That is, in the case of the polymer solution prepared from the 1.2×10^5 molecular weight polyimide, the interaction between the solvent and the polyimide was relatively strong and might have suppressed the evaporation of the solvent. In contrast, the evaporation of the solvent prepared from the 4.1×10^5 molecular weight polyimide might have been facilitated because of the weak interaction between the solvent and the polyimide.

In addition, to understand the skin layer formation, the phase separation (demixing) of the polymer induced by the solvent and nonsolvent has to be considered.^{22,23} In the wet phase-inversion process, the thermodynamic properties of the polymer solution provide some information on the phase separation. That is, the mass transfer, which is expressed by the exchange rate of the solvent/nonsolvent at the interface between the polymer solution and the coagulation bath, determines the membrane structure. The apparent diffusion coefficient exchanged between the casting polymer solution and coagulation medium was calculated from the Tyn–Calus equation.²⁴ The diffusion coefficient is one of the

TABLE VI
Apparent Cloud-Point Time During the Dry Process at Room Temperature

M_w	Cloud-point time (s)
1.2×10^5	92
2.6×10^5	58
4.1×10^5	55

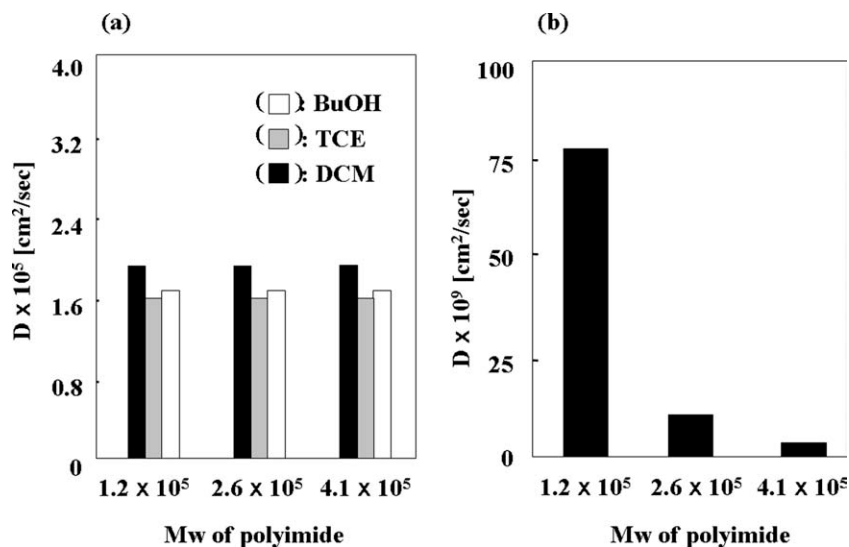


Figure 4 (a) Apparent diffusion coefficients (D' s) of BuOH, TCE, and DCM in pure MeOH and (b) apparent diffusion coefficient (D) of MeOH in the polyimide solution.

important factors in elucidating the formation mechanism of the asymmetric membrane and can provide useful thermodynamic and kinetic information.

Figure 4 shows the results of the apparent diffusion coefficient of the solvent in the casting polymer solution and with the nonsolvent as the coagulation medium at 25°C, as calculated with the following equation:²⁴

$$D_{AB} = 8.93 \times 10^{-8} (V_B^{0.267} / V_A^{0.433}) \times (T / \eta_B) (\sigma_B / \sigma_A)^{0.15} \quad (5)$$

where D_{AB} (cm²/s) is the diffusion coefficient of solute A at a low concentration in solvent B; V_A and V_B are the molar volumes of solute A and solvent B at their normal boiling temperature (cm³/mol), respectively; T (K) is the temperature; η_B (cP) is the viscosity of solvent B; and σ_A and σ_B (dyne/cm) are the surface tensions of A and B, respectively.

As is apparent from Figure 4(a), the apparent diffusion coefficients of the solvents, DCM, TCE, and BuOH, in pure MeOH as the coagulation medium were not dependent on the molecular weight of the polyimide and were almost constant. The diffusion coefficient of DCM in pure MeOH had the highest value, which was responsible for the small molar volume of DCM. However, there were hardly any differences in the diffusion coefficient among DCM, TCE, and BuOH. On the other hand, as is apparent from Figure 4(b), the apparent diffusion coefficient of MeOH as the coagulation medium in the casting polymer solution significantly depended on the molecular weight of the polyimide and decreased with increasing molecular weight. In particular, the diffusion coefficient in the polymer solution prepared from the 1.2×10^5 molecular weight polyimide had

a value 20 times higher than that prepared from the 4.1×10^5 molecular weight polyimide. This was because the viscosity of the polymer solution had a significant influence on the diffusion coefficient. We concluded that, in the wet phase-inversion process, the exchange of solvent and nonsolvent on the surface of the asymmetric membrane prepared from the 1.2×10^5 molecular weight polyimide occurred rapidly so that the thinner skin layer was formed.

In addition, we investigated the influence of a wet phase-inversion process on the surface formation with the cloud measurement. The polyimide solutions were cast on a glass plate with a doctor blade and then air-dried for 30 s at room temperature. After the dry process, the membranes were coagulated in MeOH, and we measured the apparent cloud time from the time when the initially clear membrane visually became cloudy during the wet phase-inversion process. The cloud times determined from 1.2×10^5 , 2.6×10^5 , and 4.1×10^5 molecular weights were 10, 11, and 16 s, respectively, and the time increased with increasing molecular weight. In the wet process, the cloud time was closely related to the exchange rate between the solvent and nonsolvent, and a short time produced instantaneous phase separation in the polymer solution. The trend of the cloud time determined from the wet process was similar to that of the apparent diffusion coefficient of MeOH as the coagulation medium in the casting polymer solution. That is, the exchange for the polyimide solution prepared from the 1.2×10^5 molecular weight occurred rapidly so that the instantaneous phase separation of the polymer was concluded to be induced.

The SEM micrographs also demonstrated a difference in the phase separation between the 1.2×10^5

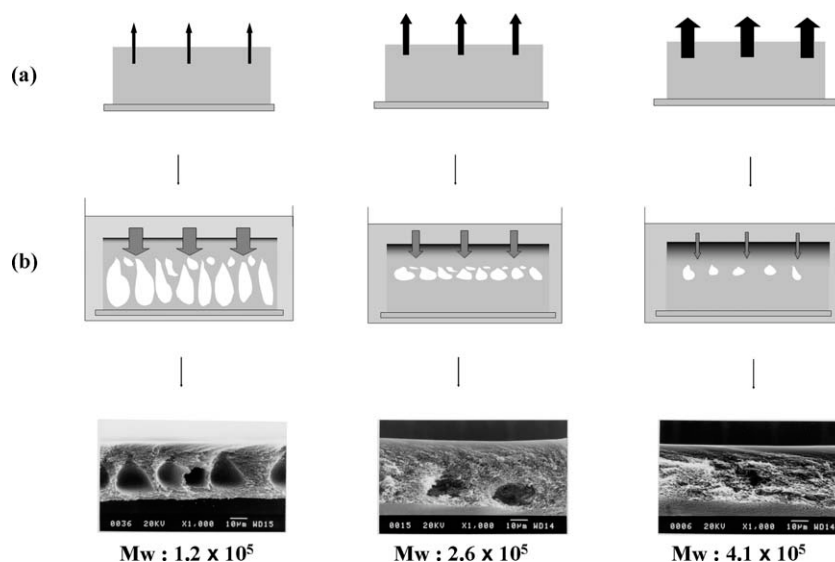


Figure 5 Formation mechanism of the asymmetric membranes made from different molecular weights: (a) dry and (b) wet processes.

and 4.1×10^5 molecular weight polyimides. The casting polymer solution prepared from the 4.1×10^5 molecular weight polyimide caused a considerable delay time in the phase separation so that the asymmetric membrane was concluded to show a spongelike structure. In contrast, in the case of the polymer solution from the 1.2×10^5 molecular weight polyimide, the delay time decreased so that the phase separation instantaneously occurred, and the asymmetric membrane was determined to form spongelike structures characterized by the presence of finger voids.

Figure 5 shows the formation mechanism of the asymmetric polyimide membranes prepared from the different molecular weight polyimides. In the dry process, the evaporation of the solvent prepared from the 4.1×10^5 molecular weight polyimide was facilitated because of the weak interaction between the solvent and the polyimide, compared to that prepared from the 1.2×10^5 molecular weight polyimide, as shown in Figure 5(a). In addition, in the wet process, the diffusion coefficient in the polymer solution prepared from the 1.2×10^5 molecular weight polyimide had a value 20 times higher than that prepared from the 4.1×10^5 molecular weight polyimide, as shown in Figure 5(b). Consequently, we concluded that the solvent evaporation in the dry phase-inversion process and the nonsolvent diffusion in the wet process were important factors in determining the formation of the asymmetric membrane. Although we have not yet paid attention to the influence of the molecular weight of the polymer on the formation of the asymmetric membrane, in this study, we found that the influence of the molecular weight of the polymer for the membrane formation was not negligible.

CONCLUSIONS

In this article, we reported the influence of the polyimide molecular weight on the structure and the gas permeation properties of the asymmetric polyimide membranes made by the dry-wet phase-inversion process. The asymmetric membranes made from the low-molecular-weight polyimide had spongelike structures characterized by the presence of finger voids, whereas the membrane made from the high-molecular-weight polyimide had only a spongelike structure. In addition, the apparent skin layer thickness of the asymmetric membrane increased with increasing molecular weight. These findings indicate that the molecular weight of the polyimide influenced the phase separation of the casting polymer solution and determined the membrane formation of the asymmetric membrane. In particular, the solvent evaporation in the dry phase-inversion process and the nonsolvent diffusion in the wet process were important factors that determined the formation of the asymmetric membrane.

References

1. Jansena, J. C.; Buonomenna, M. G.; Figolia, A.; Driolia, E. *Desalination* 2006, 193, 58.
2. Ismail, A. F.; Yaacob, N. *J Membr Sci* 2006, 275, 151.
3. Jansen, J. C.; Macchione, M.; Oliviero, C.; Mendichi, R.; Ranieri, G. A.; Drioli, E. *Polymer* 2005, 46, 11366.
4. Kazama, S.; Sakashita, M. *J Membr Sci* 2004, 243, 59.
5. Pinnau, I.; Hellums, M. W.; Koros, W. J. *Polymer* 1991, 32, 2612.
6. Pinnau, I.; Wind, J.; Peinemann, K. V. *Ind Eng Chem Res* 1990, 29, 2028.
7. Pinnau, I.; Koros, W. J. *J Membr Sci* 1992, 71, 81.
8. Pinnau, I.; Koros, W. J. *Znd Eng Chem Res* 1991, 30, 1837.

9. Kawakami, H.; Mikawa, M.; Nagaoka, S. *J Appl Polym Sci* 1996, 62, 965.
10. Kawakami, H.; Mikawa, M.; Nagaoka, S. *J Membr Sci* 1997, 137, 241.
11. Kawakami, H.; Mikawa, M.; Nagaoka, S. *Macromolecules* 1998, 31, 6636.
12. Niwa, M.; Kawakami, H.; Nagaoka, S.; Kanamori, T.; Shinbo, T. *J Membr Sci* 2000, 171, 253.
13. Kawakami, H.; Nakajima, K.; Shimizu, H.; Nagaoka, S. *J Membr Sci* 2003, 212, 195.
14. Mikawa, M.; Nagaoka, S.; Kawakami, H. *J Membr Sci* 2002, 208, 405.
15. Kawakami, H.; Nakajima, K.; Nagaoka, S. *J Membr Sci* 2003, 211, 291.
16. Kawakami, H.; Anzai, J.; Nagaoka, S. *J Appl Polym Sci* 1995, 57, 789.
17. Kawakami, H.; Takahashi, T.; Nagaoka, S.; Nakayama, Y. *Polym Adv Technol* 2001, 12, 244.
18. Niwa, M.; Nagaoka, S.; Kawakami, H. *J Appl Polym Sci* 2006, 100, 2436.
19. Mulder, M. H. V.; Smolders, C. A. *J Membr Sci* 1984, 17, 289.
20. Kok, C. M.; Rudin, A. *J Appl Polym Sci* 1982, 27, 353.
21. Kim, J. Y.; Lee, H. K.; Baik, K. J.; Kim, S. C. *J Appl Polym Sci* 1997, 65, 2643.
22. Wijmans, J. G.; Kant, J.; Mulder, M. H. V.; Smolders, C. A. *Polymer* 1985, 6, 1539.
23. Van de Witte, P.; Dijkstra, P. J.; van den Berg, J. W. A.; Feijen, J. *J Membr Sci* 1996, 117, 1.
24. Van't Hof, J. A.; Reuvers, A. J.; Boom, R. M.; Rolevink, H. H. M.; Smolders, C. A. *J Membr Sci* 1992, 70, 17.