Preparation of Novel Fluorinated Block Copolyimide Membranes for Gas Separation

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ABSTRACT: We synthesized novel fluorinated block copolyimides with various diamine compositions and block chain lengths by chemical imidization in a two-pod procedure. We describe the gas-transport properties of the novel block copolyimide membranes. We demonstrate that the gas-transport properties of the copolyimide membranes strongly depended on the block chain lengths. The gas permeabilities of the copolyimide membranes increased with increasing block chain length, and the gas selectivities increased with decreasing lengths. We clarify that the gas diffusivity of the block copolyimide membrane dominated the gas-transport properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2436–2442, 2006

Key words: block copolymers; chain; gas separation; membranes; polyimides

INTRODUCTION

Polymer membranes are considered an effective technology for the separation of gaseous mixtures due to their high separation efficiency, low operating costs, and simple operation. The development of novel polymer membranes with even higher gas permeabilities and selectivities has received a lot of attention.[1,2] Gas permeation through a polymer membrane not only is a function of the chemical structure of polymers but also is determined by the morphology or the domain structure formed on the membrane. Particularly, for block copolymers or miscible blends of polymers, their gas permeations are affected by the domain size of micrometers or nanometers formed on the membrane or the extent of the interactions between the component polymers.[3,4] In this study, we synthesized novel fluorinated block copolyimide membranes. Both the gas-transport properties and microstructures of the membranes were investigated.

Polyimide as a glassy polymer has been recognized as one of the most promising potential candidates as a gas-separation material.[5–7] In general, the polyimide is obtained from the precursor condensed from two monomers of dianhydride and diamine moieties, and the gas-transport properties through the polyimide membrane have been investigated. In contrast, there has been little attention given to the gas-transport properties of copolyimide membranes, and the polyimide reported in previous studies concerning the membranes was a random copolymer.[6,8,9]

On the other hand, in the microphase-separated states, block copolymers are known to lead to unique morphologies, such as a cylinder or sphere, due to their molecular architecture. There have also been a few studies concerning block copolyimides that reported the effects of the monomer structure and the length of the block chains on the thermal and chemical stability or mechanical properties of the copolyimide.[10,11] However, little has been elucidated about the gas-transport properties through a block copolyimide membrane.

In this study, we examined the gas-transport properties of novel fluorinated block copolyimide membranes. We considered that the block chain length would influence the morphology or domain formed on the membrane and would have an impact on the gas permeability.

EXPERIMENTAL

Materials

2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from the Clariant Co. (Shizuoka, Japan) and was purified by sublimation before use. 2,2′-Bis(4-aminophenyl)hexafluoropropane (6FAP) was purchased from the Central Glass Co. (Saitama, Japan) and was recrystallized twice in a methylene chloride solution before use. 2,4,6-Trimethyl-1,3-phenylenediamine (3MPA) was purchased from the Tokyo Kasei Co. (Tokyo, Japan) and was purified by recrystallization in a hexane solution.
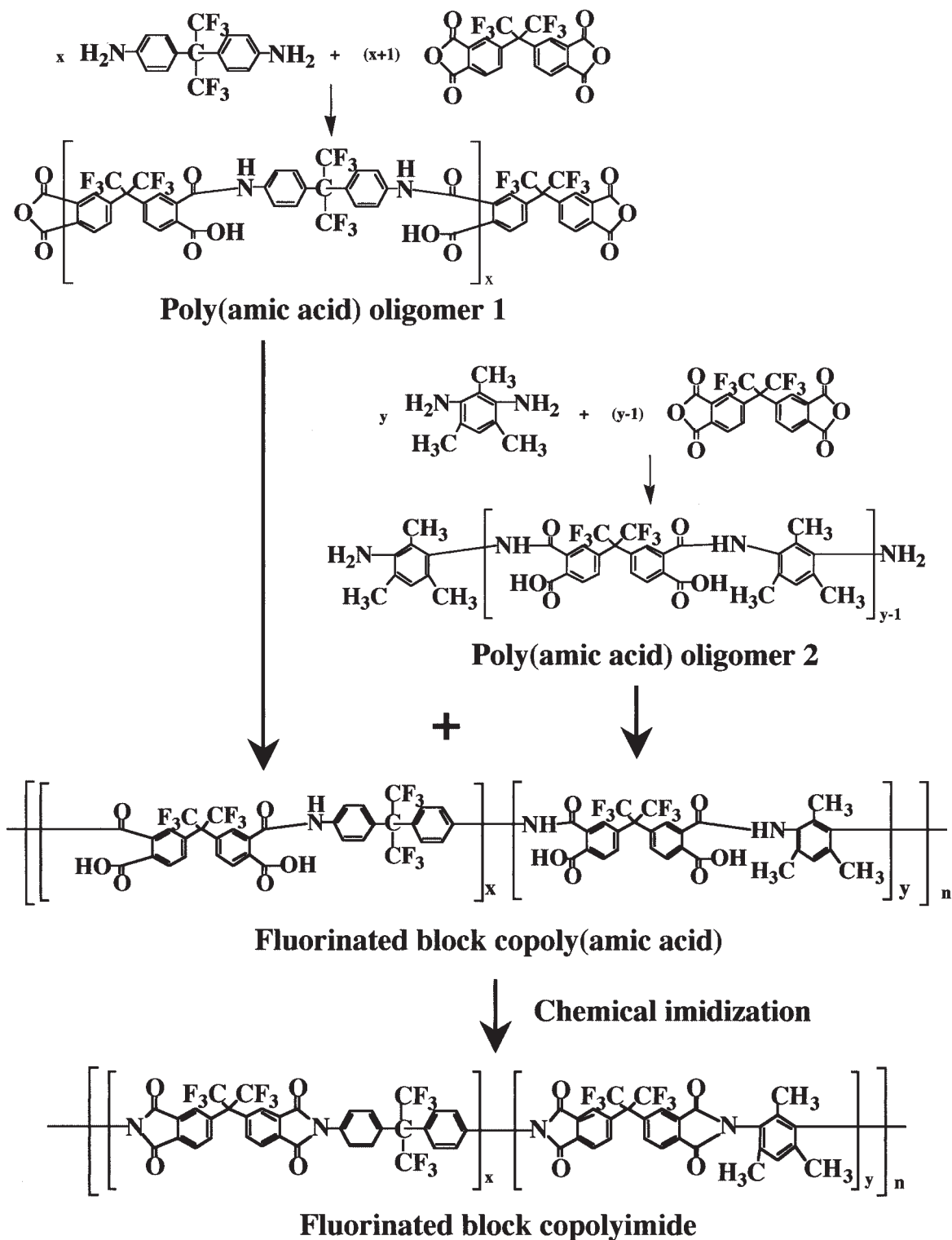
Scheme 1 Two-pod synthesis procedure of the block copolyimide.

Syntheses of the fluorinated homopolyimide, random copolyimide, and block copolyimides

Two fluorinated polyimide homopolymers were synthesized by the chemical imidization of poly(amic acid) precursors as reported in previous articles.[12,13]

The fluorinated random copolyimides were also prepared by the same method as described for the homopolyimide preparation and were derived from equimolar amounts of the dianhydride (6FDA) and diamines (6FAP/3MPA = 50/50 mol %).

Type	6FAP/3MPA	X/Y	Oligomer 1	Oligomer 2	Experimental X/Y
Block	1:1	5:5	7,500	4400	10:8
Block	1:1	10:10	9,500	6700	13:12
Block	1:1	20:20	16,600	8800	22:15

The fluorinated block copolyimides were synthesized by the two-pod procedure, as described in Scheme 1.[10] In one flask, the dianhydride-terminated poly(amic acid) oligomers were prepared by the reaction of 6FAP and a calculated excess of 6FDA in N,N'-dimethylacetamide. In another flask, the diamine-terminated poly(amic acid) oligomers were prepared from 6FDA and an excess of 3MPA. After 12 h, the diamine-terminated oligomer solution was added to the dianhydride-terminated oligomer to synthesize the fluorinated block copoly(amic acid). After stirring for 24 h, the fluorinated block poly(amic acid) precursors were converted into the block copolyimide by chemical imidization with acetic anhydride and triethylamine. After a conversion of 48 h, the fluorinated block copolyimides were precipitated in methanol, washed several times with methanol, and recovered. Subsequently, the fluorinated block copolyimides were dried in a vacuum oven at 150°C for 15 h.

Preparation of the fluorinated polyimide membranes

The fluorinated polyimide membranes were prepared with a solvent-cast method. The tetrahydrofuran (THF) solution of the polyimide was carefully cast on a glass plate, and then, the plate was placed in a vacuum oven at 40°C for 10 h to slowly remove most of the solvent. After most of the solvent was removed, the membrane was stripped from the plate by submersion in warm water and then dried in a vacuum oven at 150°C for 15 h to remove any residual solvents. The thickness of the membrane was approximately 50 μm.

Characteristics of the fluorinated polyimide

The molecular weights [weight-average molecular weight (M_w) and number-average molecular weight

(M_n)] of the fluorinated polyimide was determined by gel permeation chromatography (detector: Jasco 830-RI monitor, Tokyo, Japan) with THF as the solvent. A flow rate of 1.0 mL/min was used, and the polyimide was dissolved in THF at a concentration of 0.005 wt %. We estimated the molecular weights by comparing the retention times on a column (Shodex KF-805L, Tokyo, Japan) to those of standard polystyrene.

The density of the polyimide membranes was measured with a density gradient column at 25°C. The glass-transition temperatures (T_g's) of the polyimides were measured by differential scanning calorimetry (DSC; Seiko DSC200, SSC/5200H, Tokyo, Japan). The samples were enclosed in an aluminum pan with a cover and were heated at 10°C/min under a 40-mL/min flowing nitrogen atmosphere.

The fractional free volume (V_f) of the polyimide was calculated with the following equation:

$$V_f = \left(\frac{V - V_0}{V} \right) \qquad (1)$$

where V is the specific volume calculated from the measured density and V_o is the occupied chain volume of the polymer. The occupied volume was estimated from the van der Waal's volume (V_w) according to the equation:

$$V_0 = 1.3 V_w \qquad (2)$$

where V_w was calculated with the group contribution method of Bondi.[5]

Surface characterization of the fluorinated polyimide membranes

The surface morphology of the fluorinated polyimide membrane was visualized with atomic force micros-

Polyimide	Type	Molar ratio	X/Y	M_w	M_w/M_n
6FAP-b-3MPA (5:5)	Block	1:1	5:5	52,000	2.2
6FAP-b-3MPA (10:10)	Block	1:1	10:10	39,000	2.4
6FAP-b-3MPA (20:20)	Block	1:1	20:20	106,000	2.6
6FAP-r-3MPA	Random	1:1	—	150,000	3.5
6FDA–6FAP	Homo	1:0	—	480,000	2.3
6FDA–3MPA	Homo	0:1	—	491,000	2.4

TABLE III
Physical Properties of the Fluorinated Polyimides and Random and Block Copolyimides

Polyimide	Type	Density (g/cm³)	T_g (°C)
6FAP-*b*-3MPA (5:5)	Block	1.385	365
6FAP-*b*-3MPA (10:10)	Block	1.393	318,368
6FAP-*b*-3MPA (20:20)	Block	1.422	313,374
6FAP-*r*-3MPA	Random	1.410	348
6FDA–6FAP	Homo	1.472	310
6FDA–3MPA	Homo	1.332	383

copy (AFM; SPI3700, Seiko, Tokyo, Japan) in air at room temperature.[14] Standard Si_3N_4 cantilevers (SN-AF01, Seiko, Tokyo, Japan), 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 at a constant scan speed of 2 Hz.

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%. Polyimide membranes with an area of 0.7065×10^{-3} m² were mounted in a stainless steel permeation cell.[15] The gas permeability coefficients at 35°C and 76 cmHg were determined with a high-vacuum apparatus (Rika Seiki, Inc., K-315 H, Tokyo, Japan). The pressures on the upstream and downstream sides were detected with a Baratron absolute pressure gauge. The error in the permeability measurement was estimated to be less than 5%.

The permeation parameters were calculated from the diffusion time lags (θ's) with

$$D = L^2/6\theta \qquad (3)$$

where D is the diffusion coefficient and L is the membrane thickness. The solubility coefficient (S) was calculated from the permeability coefficient ($P = DS$).

RESULTS AND DISCUSSION

Characteristics of the fluorinated block copolyimides

Fluorinated block copolyimides with the different block chain lengths were synthesized by chemical imidization from the precursor, as shown in Scheme 1. The molecular weights of the dianhydride-terminated poly(amic acid) oligomers (oligomer 1) and the diamine-terminated poly(amic acid) oligomers (oligomer 2) are shown in Table I. The experimental X and Y values (X: molecular weight of oligomer 1, Y: molecular weight of oligomer 2) calculated from oligomers 1 and 2 were not consistent with the theoretical values. Table II shows the total molecular weight and poly-

dispersity values of the block polyimides. The degree of imidization of the block copolyimides was determined by ^{1}H-NMR spectroscopy. The results of the ^{1}H-NMR spectroscopy show that the block polyimides synthesized by the chemical imidization were completely imidized (data not shown). The block copolyimide was soluble in chloroform, dimethyl sulfoxide, N,N'-dimethylacetamide, N,N-dimethylformamide, and THF. The membranes were optically clear and mechanically stable.

Table III shows the density and T_g values of the block copolyimides. The density of the copolyimides increased with increasing X and Y values. On the other hand, the DSC measurements of 10:10 and 20:20 6FAP-*b*-3MPA showed two distinct T_g's around 310 and 370°C, whereas 5:5 6FAP-*b*-3MPA had one T_g. Interestingly, 10:10 and 20:20 6FAP-*b*-3MPA exhibited poor miscibility, whereas 5:5 6FAP-*b*-3MPA had good miscibility.

Figure 1 shows the AFM images of the top surface of the polyimide membranes. To observe the surface morphology of the membrane in detail, we measured the AFM images of 5:5 6FAP-*b*-3MPA, the random copolyimide, and the homopolyimide membranes with a scan area of 500×500 nm. On the other hand, the images of the 10:10 and 20:20 6FAP-*b*-3MPA membranes were 5×5 and 10×10 μm, respectively. One interesting aspect at the surface was that the domain structure formed on the 20:20 6FAP-*b*-3MPA membrane exhibited a regular morphology. We believe that microphase separation in 20:20 6FAP-*b*-3MPA with the longer block chain occurred.

Gas-transport properties of the fluorinated block copolyimide membranes

Table IV shows the gas permeability coefficients and gas selectivities of the copolyimide membranes at 76 cmHg and 35°C. In general, the gas permeability coefficients of the copolymer membranes are estimated with the semilogarithmic additivity rule[16]:

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \qquad (4)$$

where ϕ_I is the volume fraction and subscripts 1 and 2 refer to the two component polymers. The gas permeabilities of the 20:20 6FAP-*b*-3MPA and 6FAP-*r*-3MPA membranes were slightly greater than those calculated from the semilogarithmic additivity rule, whereas the gas permeabilities of the 5:5 and 10: 10 6FAP-*b*-3MPA membranes decreased when compared with those calculated from the semilogarithmic equation (data not shown). For the miscible blends, it has been demonstrated that the extent of the interactions between the component polymers influence the gas-transport properties[17] and that the stronger interactions are the permeability coefficients of the blends that closely fol-
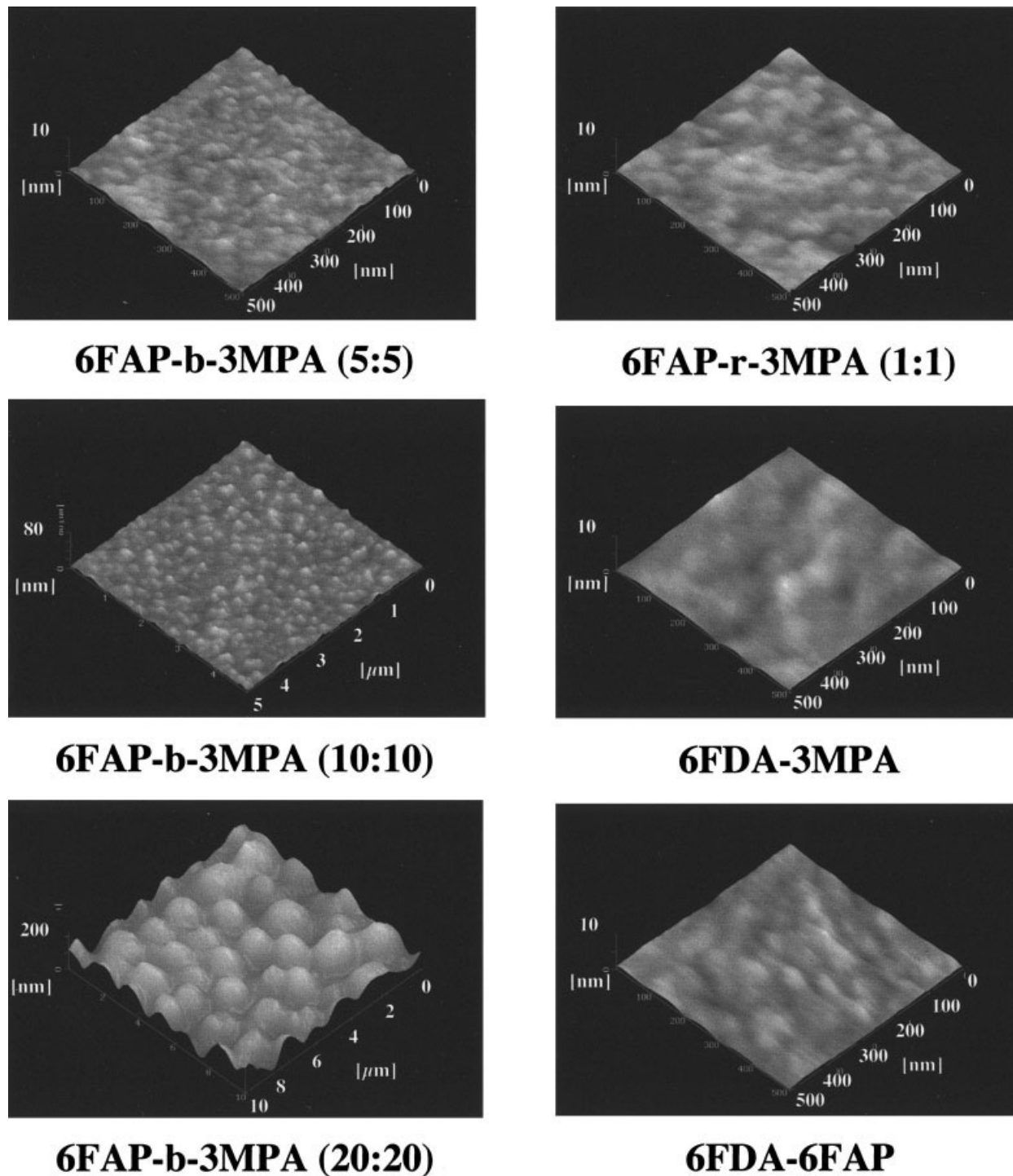
6FAP-b-3MPA (5:5)

6FAP-r-3MPA (1:1)

6FAP-b-3MPA (10:10)

6FDA-3MPA

6FAP-b-3MPA (20:20)

6FDA-6FAP

Figure 1 Three-dimensional AFM images of the polyimide membranes.

low or are below the values calculated from the semilogarithmic equation.[18] Therefore, the interactions between the component polymers in the 5:5 and 10:10 6FAP-*b*-3MPA membranes may have been relatively strong. However, 10:10 6FAP-*b*-3MPA, having two T_g's, may not have been a miscible copolymer. With further research, we will elucidate the phase separation behavior observed for the fluorinated block copolyimide membrane.

On the other hand, the gas selectivities of the copolymer membranes were estimated with the following equation:

$$\ln\left(\frac{P_A}{P_B}\right) = \phi_1 \ln\left(\frac{P_A}{P_B}\right)_1 + \phi_2 \ln\left(\frac{P_A}{P_B}\right)_2 \tag{5}$$

where P_A and P_B were permeability coefficients for gas A and gas B.

TABLE IV
Gas Permeability Coefficients [× 10^{10} cm³ (STP) cm³/cm² s Hg] and Permeability Selectivities of the Fluorinated Polyimides and Random and Block Copolyimides

Polyimide	P_{O_2}	P_{O_2}/P_{N_2}	P_{CO_2}	P_{CO_2}/P_{CH_4}
6FAP-*b*-3MPA (5:5)	12	4.5	73	36
6FAP-*b*-3MPA (10:10)	18	4.3	89	33
6FAP-*b*-3MPA (20:20)	33	4.2	158	30
6FAP-*r*-3MPA	29	4.0	158	28
6FDA–6FAP	8.0	4.7	38	33
6FDA–3MPA	100	3.4	570	21

TABLE VI
Gas Solubility Coefficients [× 10^3 cm³ (STP)/cm³ cmHg] and Solubility Selectivities of the Fluorinated Polyimides and Random and Block Copolyimides

Polyimide	S_{O_2}	S_{O_2}/S_{N_2}	S_{CO_2}	S_{CO_2}/S_{CH_4}
6FAP-*b*-3MPA (5:5)	9.0	1.2	109	8.8
6FAP-*b*-3MPA (10:10)	7.5	1.3	113	8.8
6FAP-*b*-3MPA (20:20)	10	1.3	160	8.4
6FAP-*r*-3MPA	8.3	1.3	152	8.4
6FDA–6FAP	10	1.3	104	9.5
6FDA–3MPA	17	1.3	286	6.8

All the block copolyimide membranes showed positive deviations from the dashed lines, and their gas selectivities exceeded those calculated with eq. (5) (data not shown). In particular, the gas selectivities in the 5:5 6FAP-*b*-3MPA membrane exhibited the largest values among the copolyimide membranes.

Table V shows the gas diffusion coefficients and gas diffusion selectivities of the copolyimide membranes for O_2 and CO_2. The diffusion coefficients of the block copolyimide membranes decreased in the order 20:20 6FAP-*b*-3MPA > 10:10 6FAP-*b*-3MPA > 5:5 6FAP-*b*-3MPA, which was in accordance with the trend in their gas permeabilities. On the other hand, the diffusion selectivities of the block copolyimide membranes increased in the order 20:20 6FAP-*b*-3MPA < 10:10 6FAP-*b*-3MPA < 5:5 6FAP-*b*-3MPA. The trends in their diffusion selectivities were similar to those of their gas selectivities.

Table VI shows the gas solubility coefficients and solubility selectivities of the copolyimide membranes. In the most conventional cases of glassy polymers, the gas diffusion through the polymer membrane mainly controls the behavior of the gas permeability of the polymer. It was clear that the difference in the solubility coefficient among the block copolyimide membranes was small when compared with that of the diffusion value and that in particular, the solubility selectivities were independent of the block chain length of the copolyimides and were almost constant. Thus, these results indicate that the diffusion coefficient and the diffusion selectivity of the block copoly-

imide membrane were the principal factors that dominated the gas-transport properties.

The most interesting results obtained in this study were that the block chain lengths of the fluorinated block copolyimides had a significant influence on both their gas-transport properties and characteristics. As apparent from the results shown in Table III, a difference in the block chain lengths of the block copolyimides influenced on their physical properties. The density of the block copolyimide increased with increasing block chain length. In addition, the calculated V_f''s of 5:5 6FAP-*b*-3MPA, 10:10 6FAP-*b*-3MPA, and 20:20 6FAP-*b*-3MPA were 0.196, 0.191, and 0.175, respectively, and V_f decreased with length. When one predicts from these results, the gas permeability coefficients in the block copolyimide membranes should decrease in the order 5:5 6FAP-*b*-3MPA > 10:10 6FAP-*b*-3MPA > 20:20 6FAP-*b*-3MPA. However, the gas permeability through the block copolyimide membranes exhibited completely opposite behavior, as shown in Table IV, and 20:20 6FAP-*b*-3MPA, with the smallest V_f value among the block copolyimide membranes, showed the highest gas permeability coefficients. In addition, the gas selectivities of 5:5 6FAP-*b*-3MPA, with the largest V_f value, exhibited the highest values.

On the basis of the AFM and DSC results, the domain structures formed on the block copolyimide membranes appeared to show a difference among 5:5 6FAP-*b*-3MPA () and 10:10 and 20:20 6FAP-*b*-3MP. In particular, as shown for the AFM and T_g results, the microphase separation in the 20:20 6FAP-*b*-3MPA membrane might have increased the gas permeability and decreased the gas selectivity. The physical properties, such as the density or the free volume of the polymer, are well known to determine the gas-transport properties of the polymer membrane. However, the free volume distribution formed in the polymer membrane is also one of the important factors that dominates gas-transport properties. The fluorinated block copolyimide may have had a block-chain-length-dependent free volume distribution. Lin et al.[9] also reported that the gas-transport properties of the random copolyimide membranes did not depend on V_f. However, the previous arguments require valida-

TABLE V
Gas Diffusion Coefficients (× 10^8 cm²/s) and Diffusion Selectivities of the Fluorinated Polyimides and Random and Block Copolyimides

Polyimide	D_{O_2}	D_{O_2}/D_{N_2}	D_{CO_2}	D_{CO_2}/D_{CH_4}
6FAP-*b*-3MPA (5:5)	1.3	3.7	6.7	4.1
6FAP-*b*-3MPA (10:10)	2.4	3.3	7.8	3.8
6FAP-*b*-3MPA (20:20)	3.3	3.2	9.9	3.6
6FAP-*r*-3MPA	3.5	3.1	10	3.3
6FDA–6FAP	8.0	3.6	3.6	3.5
6FDA–3MPA	58	2.6	20	3.0

tion based on the free volume distribution measurements of the block copolyimides. In the next step, we will elucidate the correlations between the free volume and the domain structure of the block copolyimide.

CONCLUSIONS

Novel fluorinated block copolyimides with various diamine compositions and block chain lengths were successfully synthesized by chemical imidization with a two-pod procedure. We demonstrated that the gas-transport properties of the block copolyimide membranes strongly depended on the block chain lengths. The gas permeabilities of the block copolyimide membranes increased with increasing block chain length, and the gas selectivities increased with decreasing length. This was due to the fact that the gas diffusivity of the block copolyimide membrane dominated the gas-transport properties.

The interesting results obtained in this study are that the gas permeabilities of the block copolyimide membranes were inversely correlated with V_f. In general, the gas permeability of a glassy polymer, such as a polyimide, strongly depends on V_f and increases with increasing volume. However, the gas permeability coefficients of the block copolyimide membranes were enhanced with decreasing V_f, and the gas selectivities were enhanced with increasing V_f. We considered that the block chain length in the fluorinated block copolyimide may have had an influence on the

free volume distribution, which is one of the important factors dominating gas-transport properties.

References

1. Stern, S. A. J Membr Sci 1994, 94, 1.
2. Stern, S. A.; Mi, Y.; Yamamoto, H. J Polym Sci Part B: Polym Phys 1989, 27, 1887.
3. Chiou, J. S.; Paul, D. R. J Appl Polym Sci 1987, 33, 2935.
4. Mikawa, M.; Nagaoka, S.; Kawakami, H. J Membr Sci 1999, 163, 167.
5. Wang, R.; Cao, C.; Chung, T.-S. J Membr Sci 2002, 198, 259.
6. Nakagima, K.; Nagaoka, S.; Kawakami, H. Polym Adv Technol 2003, 14, 433.
7. Burn, R. I.; Koros, W. Macromolecules 2003, 36, 2374.
8. Chun, B.-W.; Ishizu, C.; Itatani, H.; Haraya, K.; Shindo, Y. J Polym Sci Part B: Polym Phys 1994, 32, 1009.
9. Lin, W.-H.; Vora, R. H.; Chung, T.-S. J Polym Sci Part B: Polym Phys 2000, 38, 2703.
10. Oishi, Y.; Itoya, K.; Kakimoto, M.; Imai, Y. Polym J 1989, 21, 771.
11. Bender, T. P.; Wang, Z. Y. J Polym Sci Part A: Polym Chem 2000, 38, 3991.
12. Kawakami, H.; Mikawa, M.; Nagaoka, S. J Appl Polym Sci 1996, 62, 965.
13. Kawakami, H.; Mikawa, M.; Nagaoka, S. Macromolecules 1998, 31, 6636.
14. Kawakami, H.; Takahashi, T.; Nagaoka, S.; Nagayama, Y. Polym Adv Technol 2001, 12, 244.
15. Kawakami, H.; Mikawa, M.; Nagaoka, S. J Membr Sci 1996, 118, 223.
16. Barnabeo, A. E.; Creasy, W. S.; Robeson, L. M. J Polym Sci 1975, 13, 1979.
17. Paul, D. R. J Membr Sci 1984, 18, 75.
18. Kim, C. K.; Aguilar-Vega, M.; Paul, D. R. J Polym Sci Part B: Polym Phys 1992, 30, 1131.