The Effect of Morphology on Gas Permeability and Permselectivity in Polyimide Based on 3,3',4,4'-Biphenyltetracarboxylic Dianhydride and 4,4'-Oxydianiline

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ABSTRACT: The permeability and diffusion coefficients for H_2 , CO, CO_2 , and CH_4 through polyimide films based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) decreased, but their activation energies increased with decrease in specific volume, which reflected the average degree of molecular aggregation of the polymer. The changes were greater for gases with larger molecular diameters. The solubility coefficients also decreased with decrease in specific volume but the sorption enthalpies hardly changed. The decreases were hardly dependent on the molecular size of the gases and were similar to the decreases in the diffusion coefficient for H_2 . With decrease in specific volume, the permselectivity was enhanced significantly for the H_2/CO and H_2/CH_4 systems at the sacrifice of the permeability, but not for the CO_2/CH_4 system. There was no appreciable difference in the permeation properties attributed to the difference in the film-casting method.

KEY WORDS Gas Separation / Permeation / Sorption / Diffusion
Coefficient / Polyimide / Morphology / Annealing /

Polyimides with excellent thermal and mechanical durability, including polyimides based on pyromellitic dianhydride (PMDA), have attracted much attention as materials applicable to gas separation at high temperatures.^{1–9} Contrary to the fact that PMDA-based polyimides are not soluble in any solvent, the polyimides prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and aromatic diamines such as 4,4'-oxydianiline (ODA) and soluble in *p*-chlorophenol and have been successfully fabricated into asymmetric hollow fibers.⁵

In the previous paper,⁹ it was found that as-cast films of BPDA-ODA polyimide are amorphous and the films annealed above the glass

transition temperature (T_g) have some degree of ordering due to the molecular aggregation of polymer chain segments. The CO_2 sorption and transport properties of these BPDA-ODA polyimide films were influenced by morphology. The influence of morphology on the parameters in the dual-mode sorption and transport model¹⁰ was discussed in comparison with that reported for poly(ethylene terephthalate) (PET), a typical semicrystalline glassy polymer.

In this paper, the permeation experiments for H_2 , CO, CO_2 , and CH_4 through BPDA-ODA polyimide films prepared by different film-casting methods and annealed under different conditions were carried out, and the

effects of the casting methods and the morphology of the films on the permeability and permselectivity are discussed.

EXPERIMENTAL

Sample films of BPDA-ODA polyimide used in this study are listed in Table I. They were prepared by different film-casting methods and annealed under different conditions. BO-1 to BO-5 were prepared by casting a *p*-chlorophenol solution of the polyimide followed by annealing under different conditions, as described in the previous paper.⁹ BO-A1 and BO-A2 were prepared by casting a *N*-methylpyrrolidone solution of the precursor polyamic acid followed by the thermal imidization. The polyamic acid was prepared by condensation of BPDA with ODA in a *N*-methyl-pyrrolidone solution at room temperature. The polymerization solution was filtered, cast onto glass plates at room temperature, and then dried at 60°C for 12 h in a dust-free chamber. The polyamic acid films were removed from the glass plates and imidized at 230°C for 10 h in a vacuum. The polyimide films thus obtained (BO-A1) were then annealed at 290°C for 3 h under N₂ atmosphere to obtain BO-A2 sample films. The films 10–25 μm thick were usually used, while the films

50–80 μm thick were used for measurement of the diffusion coefficients for H₂.

Differential scanning calorimetry (DSC) data were measured with a Rigakudenki Thermal Analyzer at a heating rate of 20°C. The glass transition temperature (T_g) was measured by the penetration method with a Rigakudenki Thermomechanical analyzer (TMA). Wide angle X-ray diffraction (WAXD) were measured with a Rigakudenki X-ray diffractometer using Cu-K α radiation wavelength. The density was measured by the floating method using potassium iodide-water solutions with an accuracy of $\pm 0.001 \text{ g cm}^{-3}$.

The vacuum time-lag method similar to that described by Toi¹¹ was used to measure permeability and diffusion coefficients. Permeate receivers of 30, 100, and 400 cm³ in volume were used depending on the permeation rate. The pressure in the receiver was monitored with a MKS Baratron model 220BA pressure transducer having the measurement range from 10⁻³ to 10 Torr. The permeation cell was composed of a feed side, permeate side, and outside rooms.¹¹ Before each experimental run, the feed and permeate side rooms were evacuated upto 0.05 Torr and 10⁻⁵ Torr, respectively, for a period more than 10 times the diffusion time-lag in the previous experimental run. The outside room was also evacuated

Table I. Characterization of BPDA-ODA polyimide films

Samples	Preparation conditions	Density	V_f^a
		g cm^{-3}	—
BO-1	As cast (dried at 170°C, 20 h in vacuum)	1.366	0.121
BO-2	Annealed at 270°C, 3 h, in vacuum	1.403	0.097
BO-3	Annealed at 300°C, 2 h in N ₂ flow	1.409	0.093
BO-4 ^c	Annealed at 285°C, 6 h in vacuum	1.399	0.100
BO-5 ^c	Annealed at 304°C, 6 h in vacuum	1.402	0.098
Upilex-R	Commercially available ^b	1.398	0.100
BO-A1	Imidized at 230°C, 10 h in vacuum	1.375	0.115
BO-A2	Annealed at 290°C, 3 h in N ₂ flow	1.403	0.097

^a V_f is the free volume fraction calculated by the method of Bondi.

^b Ube Industries Ltd.

^c About 80 μm thick.

upto 0.05 Torr in order to make the blank leak level significantly low. The permeation experiments for H_2 , CO , CO_2 , and CH_4 were carried out at an upstream pressure of 10 atm and in the temperature range from 25°C to 110°C at a blank leak rate of less than 1/10 times the permeation rate. All data presented in this study are the average values for 2 or 3 runs. The apparent diffusion coefficient D was calculated from eq 1.

$$D = l^2 / (6\theta) \quad (1)$$

where l is film thickness and θ is diffusion time-lag. The apparent solubility coefficient S was calculated from the equation, $S = P/D$.

RESULTS AND DISCUSSION

The details of characterization of BO-1, -2, -3 and Upilex-R were reported in the previous paper.⁹ From the data of DSC, TMA, WAXD and density, it was found that BO-1 was amorphous and that BO-2, BO-3 and Upilex-R, which were annealed above T_g (270°C), had some degree of ordering due to the molecular aggregation of polymer chain segments. This drastic morphological change with the annealing above T_g was characteristically observed for the BPDA-ODA polyimide but not for BPDA-based polyimides containing sulfonyl or methylene linkage instead of the ether linkage.^{9,12} Figure 1 shows DSC curves of BO-A1 prepared by imidizing the polyamic acid films at a temperature far below T_g of the polyimide. An exothermic peak appeared at about 280°C only in the first run, being quite similar to the case of BO-1. The density of BO-A1 was only a little higher than that of BO-1. The WAXD curve of BO-A1 was broad and structureless, as shown in Figure 2. On the other hand, the WAXD curve of BO-A2 prepared by annealing BO-A1 above T_g had sharp reflections superimposed on a broad diffuse one, as shown in Figure 2, and was similar to that of BO-3. The density of BO-A2 was much higher than that of BO-A1 and the

Figure 1. DSC curves of BO-A1.

Figure 2. WAXD curves of BO-A1 and BO-A2.

same as that of BO-2. These results indicate that BO-A1 was amorphous and that BO-A2 was in a molecularly-aggregated state similar to that for BO-2 and BO-3.

Two kinds of models have been proposed for the morphology of PMDA-ODA polyimide, namely, a heterogeneous two-phase structure¹³ and a more-diffuse model.¹⁴ The morphology of BPDA-ODA polyimide has not been elucidated in detail, yet. Therefore, the specific volume (reciprocal of the density, $1/d$) was used as a measure of the average degree of molecular aggregation in the present study. The average degree of the aggregation was in the following order BO-3 > BO-2—BO-5—BO-A2 > BO-4—Upilex-R ≫ BO-A1 > BO-1. The average free-volume fraction (V_f) was calculated by the method of Bondi,¹⁵ using the density data shown in Table I.

The solubility and diffusion coefficients of

Figure 3. Relation of the permeability coefficients for H_2 , CO , CO_2 , and CH_4 in BPDA-ODA polyimide films at $50^\circ C$ to the specific volume. The open keys are for BO-1 to BO-5. The closed keys are for BO-A1 and BO-A2.

gases with high condensability in the glassy polymers are well-known to be dependent on pressure and have been described by the dual-mode sorption and transport model.¹⁰ The analysis of the gas sorption and transport properties of the glassy polymers in terms of the dual-mode model requires sorption and permeation experiments over the wide range of pressure. The purpose of this study was to investigate the influence of the film-casting methods and the morphology of the films on the gas permeability and permselectivity. Therefore, in the present study, the permeability coefficient and diffusion time-lag were measured only at an up-stream pressure of 10 atm, where pressure dependence of P for CO_2 became lower.

Figures 3, 4, and 5 show the relation of the permeability, diffusion, and solubility coefficients, respectively, for H_2 , CO , CO_2 , and CH_4 to the specific volumes of the films. The P , D , and S for each gas decreased with decrease in the specific volume. The relative decreases in P and D depended on the molecular size of the gas, while those in S hardly did so. The value of S for each gas in BO-3 was

Figure 4. Relation of the diffusion coefficients for H_2 , CO , CO_2 , and CH_4 in BPDA-ODA polyimide films at $50^\circ C$ to the specific volume. The open keys are for BO-1 to BO-5. The closed keys are for BO-A1 and BO-A2.

Figure 5. Relation of the solubility coefficients for H_2 , CO , CO_2 , and CH_4 in BPDA-ODA polyimide films at $50^\circ C$ to the specific volume. The open keys are for BO-1 to BO-5. The closed keys are for BO-A1 and BO-A2.

about 50% of the corresponding one in BO-1. The degree of decrease in S was similar to that in D for H_2 and fairly smaller than that in D for the other gases investigated.

Figure 6 shows plots of the permeability ratios P_{H_2}/P_{CO} and P_{H_2}/P_{CH_4} , versus the permeability coefficients, P_{H_2} . The gas separation properties were summarized in Table II. The permselectivity increased with decrease in P_{H_2} . On going from BO-1 to BO-3, P_{H_2} decreased by a factor of 1/5, while the permselectivity

Table II. Permeability, diffusion and solubility coefficients for H₂, and the ratios of each coefficient for H₂/CO and H₂/CH₄ in BPDA-ODA polyimide films at 50°C^a

Samples	P_{H_2}	D_{H_2}	S_{H_2}	P_{H_2}/P_{CO}	D_{H_2}/D_{CO}	S_{H_2}/S_{CO}	P_{H_2}/P_{CH_4}	D_{H_2}/D_{CH_4}	S_{H_2}/S_{CH_4}
BO-1	43.7	5.9	7.4	79	280	0.28	176	1300	0.13
BO-A1	30.4	—	—	96	—	—	232	—	—
Upilex-R	14.8	3.4	4.4	121	510	0.24	320	2900	0.11
BO-A2	11.3	—	—	135	—	—	420	—	—
BO-3	9.4	—	—	142	—	—	380	—	—

^a P is in $10^{-11} \text{ cm}^3(\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$, D is in $10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and S is in $10^{-4} \text{ cm}^3(\text{STP}) \text{ cm}^{-3} \text{ cmHg}^{-1}$.

Figure 6. Plots of the ideal separation factors for the H₂/CO and H₂/CH₄ systems versus the permeability coefficients for H₂ in BPDA-ODA polyimide films at 50 and 100°C. ○ and ●, BO-1; □ and ■, BO-A1; △ and ▲, Upilex-R; ▽ and ▼, BO-A2; ○ and ●, BO-3. The open and closed keys are at 50 and 100°C, respectively.

increased by a factor of 1.8 and 2.2 for H₂/CO and H₂/CH₄, respectively. The diffusivity ratios in Upilex-R were 1.8 and 2.2 times larger for the H₂/CO and H₂/CH₄ systems, respectively, than those in BO-1, while their solubility ratios were almost the same. Enhancement of permselectivity for these systems was found due to enhancement of the diffusivity selectivity with decrease in specific volume. Although Hoehn has reported for *F*-containing polyimides that appropriate annealing-treatment significantly enhanced the permselectivity for the H₂/CH₄ system with an appreciable increase in P_{H_2} ,³⁾ for the BPDA-ODA polyimide investigated in this study, the

Figure 7. Plots of the ideal separation factors for the CO₂/CH₄ system versus the permeability coefficients for CO₂ in BPDA-ODA polyimide films at 50, 80, and 100°C. ○, ●, and ●, BO-1; □, BO-A1; △, ▽, and ▲, Upilex-R; ▽, ▲, and ▼, BO-A2; ○, ●, and ●, BO-3. The open, semi-open, and closed keys are at 50, 80, and 100°C, respectively.

enhancement in the permselectivity was followed by significant reduction in P_{H_2} .

Figure 7 shows the relation of the permeability ratio, P_{CO_2}/P_{CH_4} , to the permeability coefficient, P_{CO_2} . The gas separation properties are summarized in Table III. The permselectivity increased only slightly with a significant decrease in P_{CO_2} . This is different from the result mentioned above for the H₂/CO and H₂/CH₄ systems. With decrease in specific volume caused by annealing, the diffusivity ratio increased only slightly and the solubility ratio hardly changed, resulting in only slight enhancement of permselectivity. Therefore, BO-1, the as-cast film and amorphous, is more suitable for the CO₂/CH₄ gas separation than the others which are in the molecularly aggregated state. A similar result has been reported for PMDA-ODA polyimide.⁷

Table III. Permeability, diffusion and solubility coefficients and the ratios of each coefficient for CO₂/CH₄ in BPDA-ODA polyimide films at 50°C^a

Samples	P_{CO_2}	D_{CO_2}	S_{CO_2}	$P_{\text{CO}_2}/P_{\text{CH}_4}$	$D_{\text{CO}_2}/D_{\text{CH}_4}$	$S_{\text{CO}_2}/S_{\text{CH}_4}$
BO-1	7.15	2.53	2.8	28.7	5.7	5.0
BO-A1	4.29	1.72	2.5	32.7	5.9	5.5
Upilex-R	1.61	0.84	1.9	34.6	7.3	5.6
BO-A2	1.01	0.70	1.5	37.5	6.7	5.6
BO-3	0.90	0.64	1.4	35.8	7.4	4.7

^a P is in $10^{-11} \text{ cm}^3(\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$, D is in $10^{-9} \text{ cm}^2 \text{ s}^{-1}$, and S is in $10^{-2} \text{ cm}^3(\text{STP}) \text{ cm}^{-3} \text{ cmHg}^{-1}$.

Table IV. Activation energies of the permeability and diffusion coefficients and sorption enthalpies for H₂, CO₂, and CH₄ in BPDA-ODA polyimide films^a

Sample	H ₂			CO ₂			CH ₄		
	ΔE_p	ΔE_D	ΔH	ΔE_p	ΔE_D	ΔH	ΔE_p	ΔE_D	ΔH
BO-1	18.0	25.4	-7.4	16.1	34.3	-18	27.7	42.5	-15
Upilex-R	18.5	26.7	-8.3	20.5	39.3	-19	34.2	48.8	-15
BO-A2	—	—	—	21.3	38.3	-17	35.1	50.9	-16
BO-3	—	—	—	22.2	39.5	-17	34.3	52.9	-19
BO-4	21.1	26.8	-6.2	—	—	—	—	—	—
BO-5	20.6	26.1	-6.1	—	—	—	—	—	—

^a ΔE_p , ΔE_D , and ΔH are in kJ mol^{-1} .

Activation energies of the permeability and diffusion coefficients, ΔE_p and ΔE_D , and sorption enthalpies ΔH are listed in Table IV. The ΔE_p for every gas increased with decrease in specific volume. This was attributed to an increase in ΔE_D with decrease in specific volume and ΔH remained constant within the experimental errors. Both the magnitude of ΔE_D and the relative increase in ΔE_D were greater for the larger penetrant molecule; that is, they were in the order of $\text{CH}_4 > \text{CO}_2 \gg \text{H}_2$. The activation energy for diffusion is regarded as the energy necessary for the formation of the so-called "holes" of which the minimum size required depends on the penetrant molecule.¹⁶ The diffusion of the larger penetrant molecule needs greater activation-energy as a result of the need of larger "holes". The experimental results indicated that the energy necessary for the formation of the larger "holes" increases significantly with decrease in the specific volume, in

the case of BPDA-ODA polyimide.

Both BO-A1 and BO-A2 may be assumed structurally more heterogeneous and richer in the so-called microvoids than BO-1 to BO-5, because the former type of sample films were prepared by the thermal imidization of the films of the precursor polyamic acid; that is, it might become more difficult with progress of the imidization for the segment chain to take more stable and more preferential structures. because of decrease in the mobility of the segment chains. If this is the case, some differences in the permeation properties between the former and latter types of the sample films should be observed. In Figures 3—5 where the permeability, diffusion, and solubility coefficients are plotted against the specific volume, the data points for each gas in these two types of the sample films are on a line, indicating that there is no appreciable difference in the permeation properties attributed to the different film-casting methods. Therefore, it is

considered that there is no appreciable difference in the morphology between these two types of sample films, except for differences in the specific volume attributed to differences in the thermal treatment conditions.

The following two different types of explanations are possible for the effect of morphology on the solubility and diffusion coefficients. One explanation is based on the one-phase model. In this case, we assume that BPDA-ODA polyimide is composed of one diffuse phase rather than two distinct phases, as proposed for PMDA-ODA polyimide as the more-diffuse model.¹⁴ Then, the V_f values shown in Table I can be used for interpreting the variation in D with the morphology as follows. According to the free-volume theory of Fujita,¹⁷ the thermodynamic diffusion coefficient D_T for a gas molecule in polymer matrix is given by eq 2.

$$D_T = RTA_d \exp(-B_d/V_f) \quad (2)$$

where R is the gas constant, T is the absolute temperature, V_f is the free volume fraction of the system, and A_d and B_d are parameters which depend on the molecular size and shape of the gas. Although the diffusion coefficients D determined in the present study are the apparent ones and dependent on pressure, especially for CO_2 and CH_4 , the correlation of D for each gas with V_f of the sample films was sought, as shown in Figure 8. The linear relation between $\ln D$ and V_f^{-1} was obtained for every gas investigated. The values of A_d and B_d were determined from straight lines obtained by eq 2, and are listed in Table V together with the molecular diameters of gases.¹⁸ Parameter B_d is related to the critical volume necessary for diffusion of a gas molecule and therefore should be larger for a gas with larger molecular diameter. This tendency is valid for the present case, as can be seen from Table V and Figure 8. Thus, significant decreases in D can be interpreted as due to those in V_f with morphology change induced by annealing above T_g .

Figure 8. Correlation of the diffusion coefficients for H_2 , CO , CO_2 , and CH_4 in BPDA-ODA polyimide films at 50°C with the free volume fraction of the films. The open keys are for BO-1 to BO-5. The closed keys are for BO-A1 and BO-A2.

Table V. Values of parameters A_d and B_d for H_2 , CO_2 , CO , and CH_4 in BPDA-ODA polyimide films and molecular diameters of gases

Gas	Diameter	$A_d \times 10^{10}$	B_d
	nm	mol J ⁻¹	—
H_2	0.27	49	0.37
CO	0.37	0.95	0.59
CO_2	0.39	1.6	0.63
CH_4	0.41	0.57	0.72

It has been reported that the solubility coefficients for gases in rubbery polymers hardly change when the specific volume is reduced by chemical or radiation-induced crosslinking, keeping the degree of the crystallinity constant.^{19,20} It has also been reported that the densification of polycarbonate films caused by the sub- T_g annealing results in a decrease in S for CO_2 , primarily due to decrease in the Langmuir capacity constant, but no appreciable decrease in the Henry's law solubility constant.²¹ Therefore, it is difficult to explain the decrease in S according to the one-phase model. However, we have recently found the trend that the Henry's law solubility constant for CO_2 is larger for an amorphous glassy polymer with a higher value of V_f .¹² The

present result might be regarded as an example of this trend. Further study is necessary.

Another explanation is based on the two phase model, where sorption and transport of penetrants are considered to occur only in the amorphous phase.²²⁻²⁴ In this case, we assume that BPDA-ODA polyimide has a heterogeneous two phase structure composed of ordered and amorphous phases, as proposed for PMDA-ODA polyimide.¹³ The decreases in S and D due to the presence of the ordered phase are expressed by eq 3 and 4.

$$S = S_a \phi_a \quad (3)$$

$$D = D_a / (\tau \cdot \beta) \quad (4)$$

where S_a and D_a are the solubility and diffusion coefficients for the penetrant in a completely amorphous polymer, ϕ_a is the amorphous volume fraction, τ is a tortuosity factor, and β is a chain immobilization factor reflecting decreased chain segmental mobility in the amorphous phase due to the proximity of the ordered phase. Equation 3 is considered to be a good approximation of gases with low condensability such as He and H₂, because of the negligible dominance of Langmuir-mode sorption.²⁴ Both the density of ordered phase and ϕ_a of each film were evaluated from the sorption data for H₂ according to eq 3, as shown in Table VI. The estimated density of the ordered phase (1.46 g cm⁻³) was 6.9% larger than that for the amorphous phase (1.366 g cm⁻³ for BO-1), but the difference between them was about 1/2 times as large as average one for typical semicrystalline polymers,²⁵⁾ suggesting fairly loose packing of the ordered phase for BPDA-ODA polyimide. Assuming the relation of $\tau = 1/\phi_a$,^{23,25} the β values were evaluated from eq 4, and are listed in Table VI. The β values for CO, CO₂, and CH₄ were much greater than unity except for BO-A1 and suggest the significant effect of the ordered phase on the chain segmental mobility in the amorphous phase. This is similar to the result for CO₂ in PMDA-ODA polyimide,⁸

Table VI. Amorphous phase fraction and chain immobilization factors for BPDA-ODA polyimide tentatively determined according to the two phases model

Samples	ϕ_a	β			
		H ₂	CO ₂	CO	CH ₄
BO-1	1.0	1.0	1.0	1.0	1.0
BO-A1	0.91	—	1.4	1.6	1.4
Upilex-R	0.67	1.0	1.8	1.8	2.2
BO-A2	0.62	—	2.0	1.8	2.2
BO-3	0.55	—	1.8	1.9	2.2
BO-4	0.66	1.1	—	—	—
BO-5	0.63	1.1	—	—	—

but in marked contrast to those reported for PET ($\beta \approx 1$).^{24,26} Thus, according to the two phase model, the decreases in D and S are interpreted as a result of the decrease in ϕ_a and the chain immobilization effect. The large chain immobilization effect for BPDA-ODA and PMDA-ODA polyimides may result from the small size of the amorphous and ordered phases.¹³

At the present, we cannot decide which of these two explanations is more applicable. Further study of the morphology is necessary.

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