Gas Permeability and Permselectivity in Homo- and Copolyimides from 3,3',4,4'-Biphenyltetracarboxylic Dianhydride and 3,3'- and 4,4'-Diaminodiphenylsulfones

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ABSTRACTS: The gas transport properties of homo- and copolyimides prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 3,3'- and 4,4'-diaminodiphenylsulfones (*m*-DDS and *p*-DDS, respectively) are investigated. With increasing fraction of *m*-DDS, the density of the polyimide films increased by 1.1% and the glass transition temperature decreased by 70 K. With increasing fraction of *m*-DDS, permeability coefficients P of H_2 and CO_2 in the film decreased to 1/3 and 1/15, while P ratios of H_2 to CO and CO_2 to CH_4 increased by 4.1 and 1.8 times, respectively, as a result of decrease in the diffusion coefficient and increase in diffusivity selectivity. These observations are interpreted in terms of changes in free volume fraction, distribution of size of free volume, and segmental mobility.
    KEY WORDS   Gas Permeability / Permselectivity / Polyimide / Copoly-
        imide / Diffusion

Polyimides have attracted much attention as membrane materials applicable to gas separations.[1,2] In the previous papers,[3-6] we reported the effects of morphology and chemical structure on gas permeability of polyimides based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA). Sykes and Clair reported the gas permeabilities of various polyimides based on pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA),[7] and pointed out that polyimides prepared from *meta*-diamines have lower permeabilities to O_2, CO_2, and water vapors than the corresponding polyimides from the *para*-diamines. A similar tendency has also been noted for *F*-containing polyimides,[8] polyesters[9,10] and poly(sulfone-amide)s.[11] Since the change in the permeability depends on the chemical structure of polymers, it is interesting to elucidate the factors controlling the permeability and permselectivity of these polymers.

In the present study, gas-transport properties of homo- and co-polyimides prepared from BPDA and 3,3'- and 4,4'-diaminodiphenylsulfones (*m*-DDS and *p*-DDS, respectively) are investigated.

EXPERIMENTAL

The polyimides used in this study were prepared by solution condensation of BPDA with diamines, as described in the previous paper.[3] The diamines were *p*-DDS, *m*-DDS, and mixtures of *p*-DDS and *m*-DDS (7/3 and 5/5 in the *p/m* ratio). The films were obtained

by casting p-chlorophenol solutions of the polyimides onto glass plates using a method described elsewhere.[3] Every film was dried at 473 K for 20 h in a vacuum prior to the permeation experiments. The films used were 10—30 μm thick.

The characterization of the films and permeation experiments were carried out by methods described elsewhere.[3-5] The permeability coefficient P and diffusion time-lag θ were measured at an upstream pressure of 10 atm and temperatures up to 403 K. The apparent diffusion coefficient D was expediently evaluated from θ as $D = l^2/6\theta$, where l is film thickness, although this equation dose not exactly hold for glassy polymers. The apparent solubility coefficient S was evaluated as $S = P/D$.

RESULTS AND DISCUSSION

The properties of BPDA–DDS polyimide films are listed in Table I. Free-volume fraction V_f was calculated by the group contribution method reported by Bondi.[12] Wide angle X-ray diffraction (WAXD) curves of these polyimide films were broad and structureless, indicating that the films were amorphous.

Glass transition temperature T_g was lower by 70 K for BPDA–m-DDS homopolyimide than for BPDA–p-DDS. In general, T_gs are lower for polymers with meta-oriented linkages than for polymers with para-oriented ones. The reason seems that meta-oriented polymers have higher configurational entropy due to larger degree of conformational freedom of the main chains than para-oriented polymers.[13] Lee has reported that T_gs of polyimides prepared from meta-diamines are 93.1 ± 3.1% as large as those from para-diamines on the average.[14] The difference in T_g in the present case is noted to be rather larger. T_gs of BPDA–DDS copolyimides were lower than the values estimated from the additive rule.

The density was higher by 1.1% for BPDA–m-DDS homopolyimide than for

Table I. Characterization of BPDA–DDS polyimide films[a]

p-DDS/m-DDS	T_g	Density	V_f
	K	g cm^{-3}	(—)
10/0	603	1.407	0.119
7/3	561	1.414	0.115
5/5	551	1.416	0.114
0/10	533	1.422	0.110

[a] For as cast films.

BPDA–p-DDS. The similar tendency has been reported for poly(ethylene phthalate)[10] and poly(phenolphthalein phthalate).[9] The difference in density was roughly twice as much for BPDA–DDS polyimides than the two types of polyesters. Among four pairs of F-containing polyimides recently-reported by Stern et al.,[8] there are two pairs having slightly higher density of the meta-oriented polymers than the para-oriented polymers. Due to lack of density data, it is still obscure whether there is the general tendency that a meta-oriented polymer has higher density and, therefore, more efficient packing than the corresponding para-oriented polymer. However, it is conceivable that the larger degree of conformational freedom of main chains of a meta-oriented polymer as compared to the para-oriented polymer may permit more efficient packing of the polymer chains in forming films.
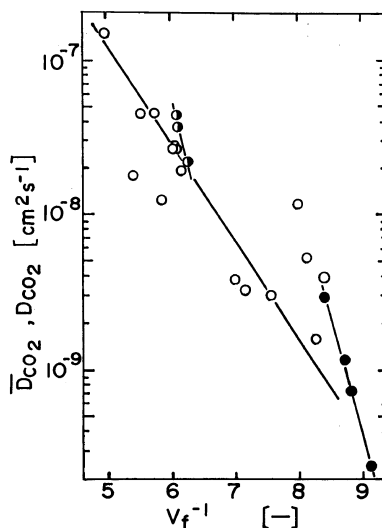
Figure 1 shows the dependence of permeability coefficients in BPDA–DDS polyimide films on the fraction of m-DDS. On going from BPDA–m-DDS to BPDA–p-DDS homopolyimides, P increased by factors of 4, 15, 18, and 27 at 323 K for H_2, CO_2, CO, and CH_4, respectively. These increases in P were attributed mainly to increases in D, while S of each gas was larger for BPDA–p-DDS than for BPDA–m-DDS by a factor of 1.5—2. The rough linear relationship between log P and fraction of m-DDS is interpreted in terms of the free volume concepts[15,16] as a result of the rough linear change in V_f with fraction of
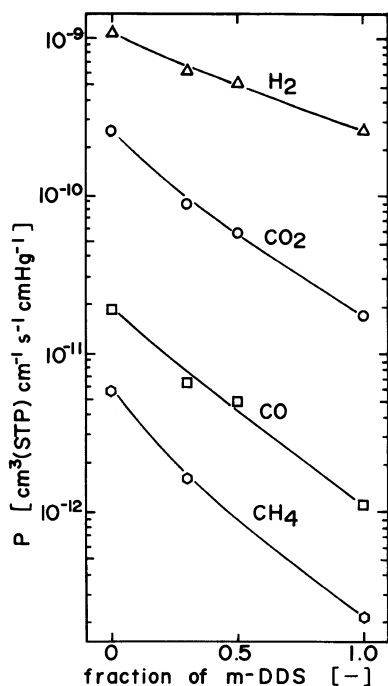
Figure 1. Dependence of permeability coefficients at 323 K and 10 atm in BPDA–DDS polyimide films on the fraction of *m*-DDS. The solid lines represent smooth lines of the experimental points.

Figure 2. Plots of diffusion coefficients (D_{CO_2} and $\bar{D}_{CO_2}$) at 308 K and 10 atm *vs.* reciprocal free-volume fractions for amorphous glassy polymers. ●, D_{CO_2} for BPDA–DDS polyimides; ◐, $\bar{D}_{CO_2}$ for poly(phenolphthalein phthalate)s; ○, $\bar{D}_{CO_2}$ for other polymers.

m-DDS.

Figure 2 shows plots of apparent diffusion coefficients D and effective diffusion coefficients $\bar{D}$ of CO_2 *vs.* V_f^{-1} for BPDA–DDS polyimides and other amorphous glassy polymers.[5] A linear correlation of log D_{CO_2} with V_f^{-1} was observed for a series of BPDA–DDS polyimide films, suggesting that decrease in D with increasing fraction of *m*-DDS is due to decrease in V_f. For BPDA–*p*-DDS polyimide, the value of $\bar{D}_{CO_2}$ was 1.3 times as large as the value of D_{CO_2}. There also appears to be a rough linear correlation of log $\bar{D}_{co_2}$ with V_f^{-1} for various polymers except for some polymers. It is noted that the correlation line of log D with V_f^{-1} for BPDA–DDS polyimides has a much larger slope than that for other polymers. A similar tendency was observed for poly(phenolphthalein phthalate)s,[9] as shown in Figure 2, although changes in $\bar{D}_{CO_2}$ and V_f were limited

to narrow ranges. In addition to the free volume fraction, other factors appear to be operative in the diffusion of a penetrant molecule through a polymer film, namely, the distribution of size of free volume and local-mode mobility of polymer chains and side groups. BPDA–*p*-DDS, BPDA-dimethyl-3,7-diamino-dibenzothiophene-5,5′-dioxide (DDBT) and PMDA-4,4′-oxydianiline (*p*-ODA) polyimides, having more rigid polymer backbone, display larger upward-deviation from the correlation of log $\bar{D}_{CO_2}$ with V_f^{-1}.[5] This suggests that these polyimides have a relatively large proportion of free-volume of sufficient size for a penetrant molecule to pass through.[5] The larger slope of the correlation line for a series of PBDA–DDS polyimides may be explained by similar consideration. An alternative explanation based on difference in segmental mobility may be probable. Pavlova *et al.* suggested that the rotation about a bond passing through a ring is forbidden if this virtual bond and valence bonds join to the ring do not lie on a straight line.[17] According to

this suggestion, Stern *et al.* recently attributed the lower permeability of F-containing polyimides from *meta*-diamines as compared to those from the *para*-diamines to the lower segmental mobility of the former.[8] Phenyl rings in the diamine moiety of the polyimides from *p*-ODA can rotate, whereas such rotation is prohibited in the polyimides from 3,3'-oxydianiline (*m*-ODA), resulting in lower segmental rotational mobility of the *meta*-oriented polyimides and therefore lower diffusivity. Assumption of reduced segmental rotational mobility of BPDA–*m*-DDS based on the similar consideration gives us a probable explanation for the higher rate of change in D_{CO_2} with V_f^{-1} for a series of BPDA–DDS polyimides; reduction of D_{CO_2} resulting from reduced segmental rotational mobility may be superimposed on the normal change in D_{CO_2} with V_f^{-1}. At the present, we have no idea which explanation is more applicable.
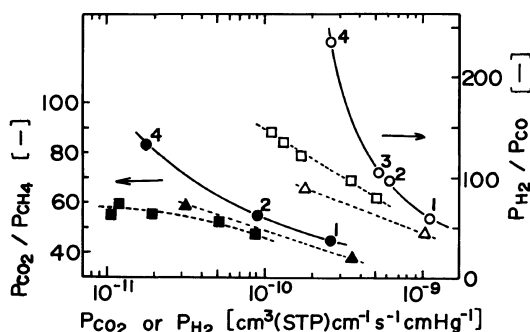
Activation energies of the permeability and diffusion coefficients, ΔE_P and ΔE_D, and sorption enthalpies ΔH are listed in Table II. Increase in ΔE_P with increasing fraction of *m*-DDS is attributed to increase in ΔE_D, while ΔH hardly varys. Increase in ΔE_D is due partly to more efficient chain packing with increasing fraction of *m*-DDS.

The differences in P between BPDA–*m*-DDS and BPDA–*p*-DDS polyimides were much larger than those reported for iso- and tere-polymers.[9,10] This is attributed to the much larger differences in D caused by larger differences in the packing density as compared to the polyesters, as shown in Figure 2. The pronounced isomerization effects observed for BPDA–DDS polyimide are probably due to the fact that they have two *meta*- or *para*-oriented linkages per a basic molecular unit, while the polyesters have one iso- or tere-oriented linkage per the unit. The CO_2 permeability ratios of *para*-oriented polyimides to the *meta*-oriented polyimides were 17, 10, 9.5, and 2.3 for BPDA–DDS, 2,2-bis(3,4-decarboxyphenyl) hexafluoropropane dianhy-

Table II. Activation energies of permeability and diffusion coefficients (ΔE_p and ΔE_D) and sorption enthalpies (ΔH) for H_2, CO_2, CO, and CH_4 in BPDA–DDS polyimide films[a]

Gas		BPDA–DDS (p)	BPDA–DDS (7/3)	BPDA–DDS (m)
H_2	ΔE_p	15	16	19
CO_2	ΔE_p	12	15	19
	ΔE_D	29	32	38
	ΔH	−17	−17	−18
CO	ΔE_p	20	24	30
	ΔE_D	36	40	44
	ΔH	−16	−16	−15
CH_4	ΔE_p	29	32	38
	ΔE_D	46	48	54
	ΔH	−17	−16	−16

[a] ΔE_P, ΔE_D, and ΔH are at 10 atm and in kJ mol^{-1}.

Figure 3. Plots of P_{H_2}/P_{CO} *versus* P_{H_2} (open keys) and P_{CO_2}/P_{CH_4} *versus* P_{CO_2} (closed keys) in BPDA–DDS (○, ●) and BPDA–ODA[4] (□, ■) polyimide films at 323 K and 10 atm, and PMDA–ODA (△, ▲) polyimide films at 308 K. 1, BPDA–DDS (p); 2, BPDA–DDS (7/3); 3, BPDA–DDS (5/5), 4, BPDA–DDS (*m*).

dride(6FDA)–ODA,[8] BTDA–ODA,[7] and PMDA–ODA[8] polyimides, respectively, at 308 K or room temperature. The ratio of BPDA–DDS polyimide was a little larger than those for others.

Figure 3 shows plots of the permeability ratios P_{H_2}/P_{CO} and P_{CO_2}/P_{CH_4} *versus* permeability coefficients P_{H_2} and P_{CO_2} in BPDA–DDS polyimide films at 323 K. With increasing fraction of *m*-DDS, P_{H_2}/P_{CO} increased by 4.1 times and P_{H_2} decreased to 1/3, while P_{CO_2}/P_{CH_4}

Table III. Permeability, diffusion, and solubility coefficients and the ratio of each
coefficient for the CO_2/CH_4 system in BPDA–DDS polyimide
films at 323 K and 10 atm[a]

p-DDS/m-DDS	P_{CO_2}	D_{CO_2}	S_{CO_2}	P_{CO_2}/P_{CH_4}	D_{CO_2}/D_{CH_4}	S_{CO_2}/S_{CH_4}
10/0	2.7	5.0	5.3	45	10.9	4.2
7/3	0.90	2.1	4.3	55	12.8	4.3
5/5	0.58	1.3	4.4	—	—	—
0/10	0.18	0.50	3.6	83	18.8	4.4

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

increased by 1.8 times and P_{CO_2} decreased to 1/15. The morphology of BPDA–ODA and PMDA–ODA polyimides can be changed by heat-treatment from amorphous state to the state having some degree of ordering due to the molecular aggregation of polymer chain segments.[3,4,18] Change in permeability and permselectivity with change in the morphology is also shown in Figure 3 for comparison. As a modification method of polyimide for membrane material, copolymerization followed by introduction of *meta*-oriented diamine moieties into *para*-oriented polymer chains prefers heat-treatment followed by the morphology change, because of larger enhancement of the permeselectivity with smaller reduction of the permeability.

Table III shows a comparison of the gas separation properties of BPDA–DDS polyimide films for the CO_2/CH_4 system. The increase in P_{CO_2}/P_{CH_4} is attributed to that in diffusivity selectivity, while solubility selectivity for each film hardly changed. BPDA–m-DDS homopolyimide having more efficient chain packing prefers separation of gas mixtures with widely different molecular diameters, such as H_2/CO system, while BPDA–p-DDS homopolyimide having less efficient chain packing prefers separation of gas mixtures with similar molecular diameters such as CO_2/CH_4 separation.

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