

# Effects of Molecular Structure on the Permeability and Permselectivity of Aromatic Polyimides

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## SYNOPSIS

Permeability coefficients of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> were measured under 10 atm at the temperature from ambient temperature up to 150°C in a series of structurally different aromatic homo- and copolyimides, which were prepared from 4,4'-oxydianiline (ODA) or 4,4'-methylene dianiline (MDA) with various aromatic dianhydrides. The study shows that the molecular structure of the polyimides strongly influences gas permeability and permselectivity. As a result, the permeability coefficients of the polyimide membranes for each gas vary by over two orders of magnitude. In general, among the polyimide membranes studied, the increase in permeability of polymers is accompanied by the decrease in permselectivity, and the MDA-based polyimide membranes have higher permeability than ODA-based ones. Among the polyimides prepared from bridged dianhydrides, the permeability coefficients to H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> are progressively increased in the order BPDA < BTDA < ODPDA ~ TDPA < DSDA < SiDA < 6FDA, while H<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> permselectivity coefficients are progressively decreased in the same order. The copolyimide membranes, which were prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SiDA), and ODA, have favorable gas separation properties and are useful for H<sub>2</sub>/N<sub>2</sub> separation applications. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Aromatic polyimides have been used in many high-technology fields as high-performance polymeric materials for their excellent thermal, mechanical, and electrical properties. For example, they can be used as insulation layers for semiconductor devices<sup>1</sup> or substrates for flexible printed circuits.<sup>2</sup> In recent years, polyimide has attracted much attention as a gas separation membrane material because of its excellent properties.<sup>3-5</sup> Polyimide asymmetric membranes, which were prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), for gas separation and dehumidification have been reported to show excellent performance under severe conditions for long-term use.<sup>6,7</sup> To develop good gas barrier and separation membrane materials, it is important to investigate the factors influencing gas permeability and permselectivity of polymers. Studies on polyimides, which were pre-

pared from pyromellitic dianhydride (PMDA),<sup>8-10</sup> (BPDA),<sup>10-13</sup> 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA),<sup>8,10,14</sup> and 2,3-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA),<sup>10,15-26</sup> indicated that diamine structure can have a large effect on gas permeability and permselectivity.

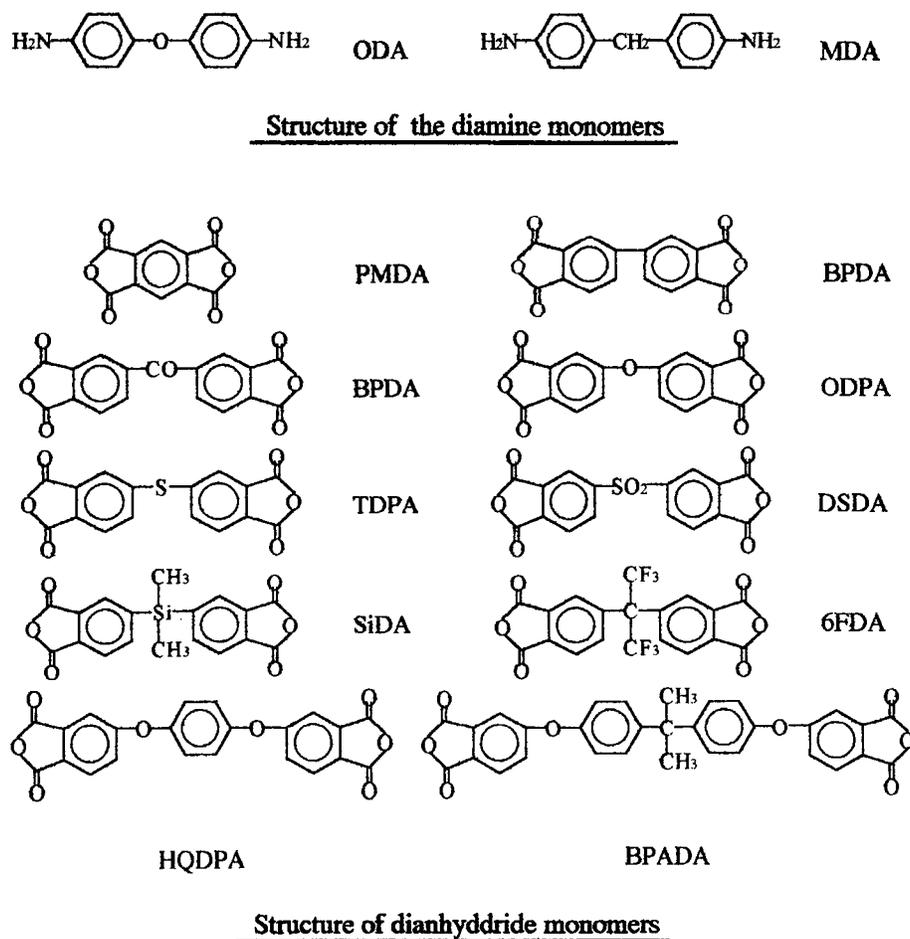
In the present study the permeability coefficients of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> through a series of aromatic polyimides prepared from 4,4'-oxydianiline (ODA) or 4,4'-methylene dianiline (MDA) with various aromatic dianhydrides were measured under 10 atm and from ambient temperature up to 150°C to investigate the effects of dianhydride monomer structure on gas permeability and permselectivity. The amorphous membranes were made by the solution casting method.

## EXPERIMENTAL

### Materials

The chemical structure of dianhydride and diamine used for this study is given in Figure 1. ODA and

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**Figure 1** Structure of the diamine and dianhydride monomers used.

MDA were obtained from Shanghai Chemical Reagent Factory (China). PMDA and BTDA were obtained from Shanghai Chemical Reagent Factory (China) and Daciel Corp. (Japan), respectively. ODPA and 6FDA were kindly supplied by Oxychem Co. (USA) and Hoeschst Corp. (Germany). BPDA, 3,3',4,4'-thiadiphthalic tetracarboxylic dianhydride (TDPA), 3,3',4,4'-biphenylsulfone tetracarboxylic dianhydride (DSDA), 1,4-bis(3,4-dicarboxyphenyl) benzene dianhydride (HQDPA), 2,2-bis[4-(3,4-dicarboxyphenoxy)-phenyl] propane dianhydride (BPADA), and (3,4-dicarboxyphenyl) dimethylsilane dianhydride (SiDA) were prepared in our laboratory. All the dianhydride and diamine monomers were finally purified by vacuum sublimation or repeat crystallization just prior to use in polymerization. The solvent *N,N*-dimethylacetamide (DMAc) was purified by drying with a 4 Å molecular sieve for one week at 30°C followed by distillation under

nitrogen atmosphere. The purity of the permeation gases used was more than 99.9%.

#### Preparation of Membranes

Polyamic acid precursors were prepared by solution condensation of an aromatic dianhydride with a stoichiometrical amount of an aromatic diamine in DMAc, according to standard procedures.<sup>27</sup> The polyamic acid solutions were filtered with sintered glass filter before casting. Membranes were cast from solution on glass plates in a controlled dust-free environment. The freshly cast membranes were then heated at about 40–50°C for 12 h to speed drying. During drying, the relative humidity in air was maintained at 20–30%. Each HQDPA-based and BPADA-based membrane was thermally imidized on the glass plates in a vacuum oven by heating at 100°C for 5 h and at 280°C for 1.5 h, and the others were thermally imidized on the glass plates in vac-

uum oven by heating at 100°C for 5 h and at 300°C for 1.5 h. After cooling to below 50°C, polyimide membranes were removed from the glass plates by stripping in a heat water bath and then dried in a vacuum oven at 150°C for one week. The polyimide membranes obtained generally were about 0.0035 cm in thickness.

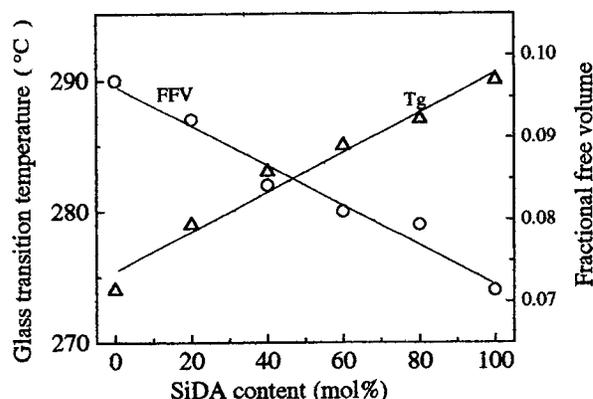
### Apparatus and Procedure

Glass transition temperatures ( $T_g$ ) of the polyimides were measured using a Perkin-Elmer Series 7 differential scanning calorimetry DSC instrument in static air at 10°C/min. Densities of the polyimide membranes were determined at 25°C by the floating method using a mixed solvent of ethanol and carbon tetrachloride. Wide-angle X-ray diffraction (WAXD) measurements for the polyimide membranes were undertaken on a Philips X-ray diffractometer with  $\text{CuK}\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ . The permeability coefficients of  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  through the polyimide membranes were measured under 10 atm at ambient temperature up to 150°C. The data were taken using the manometric apparatus made in our laboratory. The procedure is similar to that described previously.<sup>28</sup>

**Table I** The Physical Properties of the Homopolyimide Membranes

Polyimide	$T_g$ (°C)	$\rho$ (g/cm <sup>3</sup> )	SFV (cm <sup>3</sup> /g)	FFV
PMDA-ODA	299	1.402	0.060	0.084
BPDA-ODA	290	1.382	0.056	0.079
BTDA-ODA	271	1.375	0.064	0.088
ODPA-ODA	260	1.376	0.066	0.091
TDPA-ODA	258	1.383	0.067	0.092
DSDA-ODA	295	1.407	0.067	0.094
SiDA-ODA	274	1.286	0.074	0.095
6FDA-ODA	296	1.431	0.068	0.097
HQDPA-ODA	256	1.370	0.063	0.086
BPADA-ODA	215	1.303	0.072	0.094
PMDA-MDA	308	1.350	0.063	0.085
BPDA-MDA	296	1.332	0.064	0.084
BTDA-MDA	280	1.346	0.067	0.090
ODPA-MDA	264	1.340	0.067	0.090
TDPA-MDA	265	1.343	0.068	0.091
DSDA-MDA	304	1.371	0.067	0.092
6FDA-MDA	297	1.408	0.068	0.096
HQDPA-MDA	259	1.334	0.066	0.088
BPADA-ODA	217	1.298	0.072	0.093

$T_g$ , Glass transition temperature;  $\rho$ , density; SFV, specific free volume; FFV, fractional free volume.



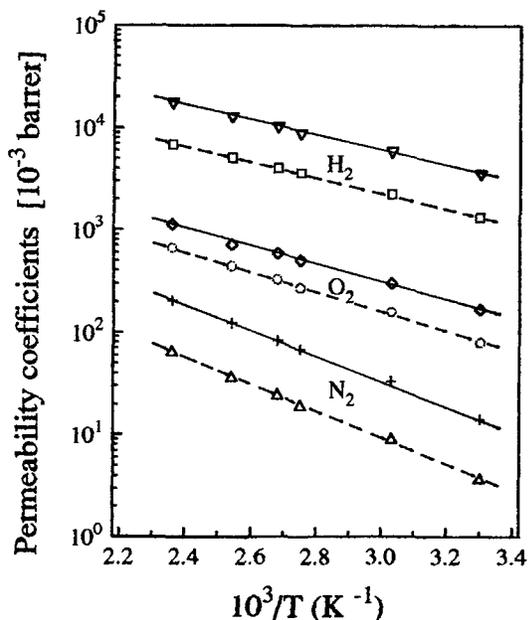
**Figure 2** SiDA content dependence of glass transition temperature and fractional free volume of the copolyimides from BPDA, SiDA, and ODA.

## RESULTS AND DISCUSSION

### Characterization of Polyimide Membranes

The physical properties of the homopolyimides studied are listed in Table I. Wide angle X-ray diffraction curves of all the polyimide membranes were broad and structureless, indicating that the membranes were amorphous. The specific free volumes (SFVs) of the polyimide membranes were estimated by the method of Lee,<sup>29,30</sup> which used the group contribution of Bondi<sup>31</sup> for calculation of van der Waals volume. The fractional free volumes (FFVs) were the ratios of the estimated specific free volume and the specific volume of the polyimides measured at 25°C. One can see from Table I that among the polyimides studied, those from rigid dianhydrides (PMDA or BPDA) have the lowest fractional free volume; the fractional free volume is increased with increases of the bridge group in double-nuclei dianhydrides; BPADA-based polyimides have larger fractional free volumes than HQDPA-based ones; and except for 6FDA-based and BPADA-based polyimides, MDA-based polyimides have a larger free-volume fraction than corresponding ODA-based ones.

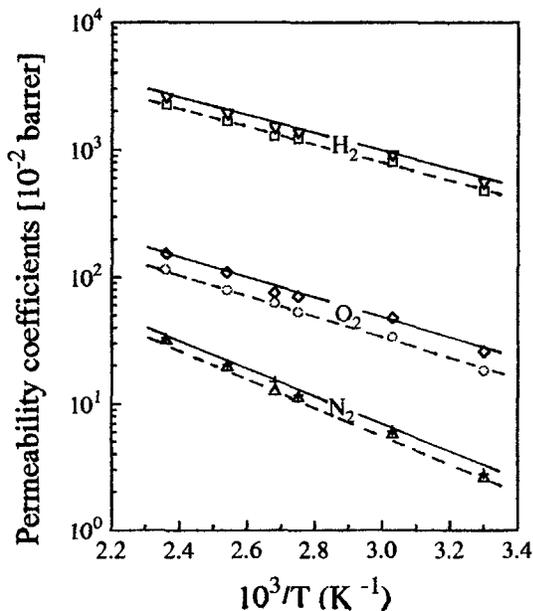
The relationship between the fractional free volume and glass transition temperature and the molecular structure of the copolyimides, which were prepared from BPDA, SiDA, and ODA, is shown in Figure 2. The fractional free volume increases with increases of the SiDA segment content in the copolyimide, while the glass transition temperatures decrease with increases of the SiDA segment content in the copolyimide.



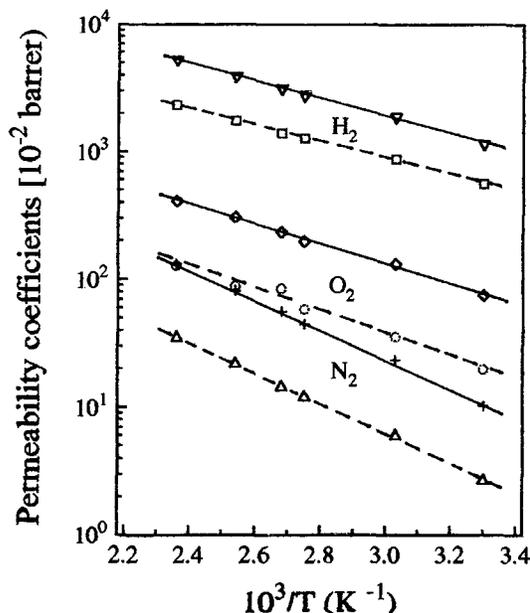
**Figure 3** Temperature dependence of the permeability coefficients of BPDA-MDA (dashed line) and BPDA-MDA (solid line) for  $H_2$ ,  $O_2$ , and  $N_2$  at 10 atm.

#### Permeability and Permselectivity

The permeability coefficients of the representative polyimide membranes for  $H_2$ ,  $O_2$ , and  $N_2$  are illustrated in the form of Arrhenius plots in Figures 2-5. Most of the measurements were carried out in



**Figure 4** Temperature dependence of the permeability coefficients of ODPA-ODA (dashed line) and ODPA-MDA (solid line) for  $H_2$ ,  $O_2$ , and  $N_2$  at 10 atm.



**Figure 5** Temperature dependence of the permeability coefficients of DSDA-ODA (solid line) and SiDA-ODA (dashed line) for  $H_2$ ,  $O_2$ , and  $N_2$  at 10 atm.

the temperature range of 30–150°C. The permeability coefficients increase almost linearly as the increase of temperature in Arrhenius plots. The permeability coefficients at 30 and 100°C and the apparent activation energies ( $E_p$ ) for the permeation of  $H_2$ ,  $O_2$ , and  $N_2$  calculated from the slopes are listed in Table II.  $H_2/N_2$  and  $O_2/N_2$  permselectivity coefficients of the polyimide membranes at 30 and 100°C are listed in Table III.

The permeability coefficient ( $P$ ) can be shown to be a product of a diffusion ( $D$ ) and a solubility coefficient ( $S$ ):

$$P = DS \quad (1)$$

where  $S$ , a thermodynamic factor, can be determined by the inherent condensability of the penetrant gas, by polymer-penetrant gas molecule interactions, and by the amount of excess volume (namely, free volume) existing in the glassy polymers; and  $D$ , a kinetic factor, can be determined by dividing the permeability coefficient by the solubility coefficient. The permselectivity coefficient, ( $\alpha_{A/B}$ ), can be expressed according to eq. (2):

$$\alpha_{A/B} = P_A/P_B = [D_A/D_B]/[S_A/S_B] \quad (2)$$

The ratio  $D_A/D_B$ , which is kinetic in nature, is known as the diffusivity selectivity; and the ratio

**Table II Gas Permeability Coefficients and Apparent Activative Energies for Gas Permeation of the Polyimide Membranes under 10 atm and 30 and 100°C**

Polyimide	$P [10^{-10} (\text{cm}^3(\text{STP}) \text{ cm})/(\text{cm}^2 \text{ s cmHg})]$						$E_p (\text{kJ/mol})$		
	30°C			100°C			H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>
	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>			
PMDA-ODA	5.89	0.496	0.059	16.8	1.53	0.312	14.1	15.1	21.9
BPDA-ODA	1.33	0.079	0.004	4.00	0.326	0.024	14.7	18.9	25.5
BTDA-ODA	3.59	0.170	0.012	10.4	0.620	0.076	14.3	17.7	24.6
ODPA-ODA	4.77	0.183	0.026	12.8	0.631	0.116	13.8	16.4	22.2
TDPA-ODA	4.68	0.198	0.021	13.6	0.660	0.119	13.9	16.3	21.9
DSDA-ODA	5.61	0.200	0.027	14.1	0.854	0.145	12.6	16.0	21.9
SiDA-ODA	11.7	0.764	0.104	31.7	2.36	0.567	13.4	15.1	21.9
6FDA-ODA	46.3	4.31	0.562	94.2	8.98	1.79	9.55	9.86	15.6
HQDPA-ODA	4.00	0.216	0.034	11.5	0.777	0.158	14.2	17.2	20.8
BPADA-ODA	8.95	0.550	0.084	24.9	2.03	0.414	13.4	16.6	22.4
PMDA-MDA	6.61	0.398	0.069	18.5	1.25	0.324	14.0	15.6	20.8
BPDA-MDA	3.60	0.168	0.014	10.4	0.591	0.083	14.2	16.9	23.8
BTDA-MDA	4.03	0.211	0.020	11.4	0.716	0.110	13.9	16.6	23.2
ODPA-MDA	5.62	0.261	0.028	15.1	0.758	0.158	13.3	16.2	23.0
TDPA-MDA	5.43	0.246	0.027	14.8	0.823	0.156	13.7	16.1	22.1
DSDA-MDA	6.32	0.296	0.032	15.8	0.972	0.181	12.6	16.0	22.7
6FDA-MDA	44.7	4.05	0.564	91.8	8.50	0.848	9.67	9.96	15.7
HQDPA-MDA	5.08	0.242	0.036	14.4	0.966	0.176	14.0	18.1	21.5
BPADA-MDA	8.31	0.501	0.076	24.3	1.78	0.378	13.4	16.9	21.2

**Table III H<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> Permselectivity Coefficients of the Polyimide Membranes under 10 atm and at 30 and 100°C**

Polymimide	$\alpha_{\text{H}_2/\text{N}_2}$		$\alpha_{\text{O}_2/\text{N}_2}$	
	30°C	100°C	30°C	100°C
	PMDA-ODA	100	55.9	8.4
BPDA-ODA	365	169	26	13
BTDA-ODA	290	136	14	8.3
ODPA-ODA	216	111	9.8	6.2
TDPA-ODA	261	111	10.1	6.3
DSDA-ODA	210	98.6	9.7	5.9
SiDA-ODA	113	56.1	7.6	4.1
6FDA-ODA	64.8	52.6	6.0	5.1
HQDPA-ODA	118	73.0	6.4	5.0
BPADA-ODA	106	60.1	6.4	4.9
PMDA-MDA	95.5	57.3	8.3	3.9
BPDA-MDA	255	123	11.9	7.2
BTDA-MDA	206	104	10.8	6.5
ODPA-MDA	202	95.6	9.0	5.4
TDPA-MDA	201	97.3	9.3	5.6
DSDA-MDA	195	87.5	9.1	5.4
6FDA-MDA	65.8	50.7	6.1	4.8
HQDPA-MDA	143	82.3	6.8	5.5
BPADA-MDA	109	66.1	6.6	4.8

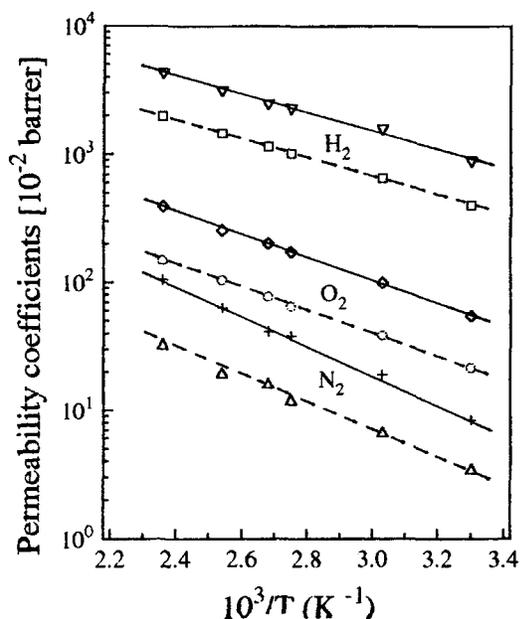
$S_A/S_B$ , which is thermodynamic in nature, is known as the solubility selectivity.  $D_A/D_B$  and  $S_A/S_B$  represent the contributions to the overall selectivity arising from differences in the diffusivities and solubilities of the penetrant  $A$  and  $B$ , respectively. As shown in Figures 2–5, the permeability coefficient of the polyimide membranes for three gases decreases, at each temperature, in the order

$$P_{\text{H}_2} > P_{\text{O}_2} > P_{\text{N}_2}$$

This is also the order of increasing kinetic molecular diameters (H<sub>2</sub>: 2.89Å, O<sub>2</sub>: 3.46Å, and N<sub>2</sub>: 3.64Å) of the penetrant gases. Hence, H<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> permselectivity coefficients of the polyimide membranes are largely controlled by the diffusivity selectivity, as is the case for other polymers.<sup>28,32,33</sup>

#### Relationship between Homopolyimide Structure and Permeability and Permselectivity

The results listed in the Tables II and III clearly show that dianhydride and diamine structure has a strong effect on the gas permeability and permselectivity of the polyimide membranes, and the effect



**Figure 6** Temperature dependence of the permeability coefficients of HQDPA-ODA (dashed line) and BPADA-ODA (solid line) for H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> at 10 atm.

of the chemical structure of the polyimides at low temperature is stronger than at high temperature. Structure variations of the dianhydrides cause polyimide membranes studied one order of magnitude range and two orders of magnitude range in permeability coefficients for H<sub>2</sub> and for N<sub>2</sub>, respectively.

According to Koros and co-workers,<sup>15</sup> the permeability and permselectivity of polyimide are mainly controlled by intersegmental packing density (fractional free volume) and intrasegmental mobility. Polyimides with a large fraction free volume have high permeability, and polyimides with low intrasegmental mobility (or high glass transition temperature) usually have high permselectivity. BPADA-

ODA membranes with the lowest fractional free volume and lower intrasegmental mobility possess the lowest permeability and the highest permselectivity, and 6FDA-ODA membranes with the largest fractional free volume and lowest intrasegmental mobility have the highest permeability and the lowest permselectivity.

The permeability coefficient of the polyimide membrane of each gas is progressively increased as the bridged dianhydride is varied from BPDA through ODPDA, TDPA, DSDA, and SiDA to 6FDA. This is also the order of increase in fractional free volume of the polyimide membranes; therefore, the fractional free volume plays a dominant role in determining the permeability change compared with a small difference in intrasegmental mobility in this case. The relative increase of permeability due to the variation of the chemical structure of the bridged dianhydride is more effective in causing an increase in the permeability of the larger penetrating gas in comparison with the smaller ones. Hence, increases in permeability of these polyimide membranes are accompanied by decreases in permselectivity. The molecular structure of ODPDA is similar to that of TDPA, with the result that the fractional free volume and intrasegmental mobility are almost the same as those of TDPA. Hence, there is almost no difference between the permeability and permselectivity of ODPDA-based polyimide membranes and those of TDPA-based ones.

Among the polyetherimides from HQDPA and BPADA, BPADA-based polyetherimides with a bulky  $-\text{C}(\text{CH}_3)_2-$  bridge group have a much larger fractional free volume and higher intrasegmental mobility compared with HQDPA-based ones. Thus BPADA-based polyetherimides have much higher permeability and lower permselectivity than HQDPA-based ones.

**Table IV** Permeability Coefficients of the Copolyimide Membranes Prepared from BPDA, SiDA, and ODA for H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> at 30 and 100°C

Polyimide	SiDA (mol %)	$P$ [ $10^{-10}(\text{cm}^3(\text{STP}) \text{ cm})/(\text{cm}^2 \text{ s cmHg})$ ]					
		30°C			100°C		
		H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>
BPADA-ODA	0	1.33	0.079	0.004	4.00	0.326	0.024
PI-8020	20	3.30	0.154	0.018	9.78	0.575	0.534
PI-6040	40	6.21	0.326	0.040	18.4	1.15	0.119
PI-4060	60	8.78	0.503	0.060	23.6	1.57	0.161
PI-2080	80	9.63	0.621	0.074	26.3	1.92	0.203
SiDA-ODA	100	11.7	0.764	0.104	31.7	2.36	0.567

**Table V**  $H_2/N_2$  and  $O_2/N_2$  Permselectivity Coefficients of the Polyimide Membranes under 10 atm and at 30 and 100°C

Polyimide	SiDA (mol %)	$\alpha_{H_2/N_2}$		$\alpha_{O_2/N_2}$	
		30°C	100°C	30°C	100°C
BPDA-ODA	0	365	169	22	13
PI-8020	20	183	90	8.8	4.8
PI-8020	40	155	76	8.5	4.7
PI-8020	60	147	73	8.4	4.7
PI-8020	80	130	64	8.4	4.5
SiDA-ODA	100	113	56	7.6	4.1

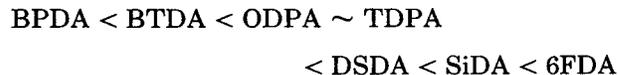
Except for 6FDA-MDA and BPADA-MDA, MDA-based polyimides have higher permeability than ODA-based ones due to the difference in fractional free volume. The free volume of 6FDA-based and BPADA-based polyimides originates mainly from the spacing of the  $-C(CF_3)_2-$  and  $-C(CH_3)_2-$  bridge group, and the volume of the  $-CH_2-$  group is larger than that of either linkage ( $-O-$ ); therefore, the fractional free volumes of 6FDA-MDA and BPADA-MDA are smaller than those of 6FDA-ODA and BPADA-ODA, respectively, with the result that 6FDA-MDA and BPADA-MDA have lower permeability than 6FDA-ODA and BPADA-ODA, respectively.

#### Relationship between BPDA/SiDA-ODA Composition and Permeability and Permselectivity

The permeability coefficients of the copolyimide membranes prepared from BPDA, SiDA, and ODA of  $H_2$ ,  $O_2$ , and  $N_2$  at 30 and 100°C are listed in Table IV, and  $H_2/N_2$  and  $O_2/N_2$  permselectivity coefficients at 30 and 100°C are listed in Table V. With the increase of an SiDA segment having a bulky  $-Si(CH_3)_2-$  bridge group, the fractional free volume of the copolyimides, which were prepared from BPDA, SiDA, and ODA, progressively increases. The result is that the permeability of the copolyimides of each gas is progressively increased with increases in the ratio of SiDA to BPDA. The composition of the copolyimides studied here has a stronger effect on the permeability of larger penetrant molecules than that of smaller ones. As a result,  $H_2/N_2$  and  $O_2/N_2$  permselectivity of those were progressively decreased with increases in the ratio of SiDA to BPDA. The effect of copolyimide composition on permeability and permselectivity is weaker at high temperatures than at low temperatures. This is similar to the case of homopolyimides.

#### CONCLUSIONS

The molecular structure of polyimides has a strong influence on the permeability coefficients of  $H_2$ ,  $O_2$ , and  $N_2$ , with results for some polyimides varying two orders of magnitude from that of others. The effect of the molecular structure of polyimides on permeability and permselectivity at high temperatures is weaker than at low temperatures. Among the polyimides prepared from bridged dianhydrides, the permeability coefficients of  $H_2$ ,  $O_2$ , and  $N_2$  are progressively increased in the order



$H_2/N_2$  and  $O_2/N_2$  permselectivity coefficients are progressively decreased in the same order. The polyetherimides with flexible segments, which were prepared from HQDPA and BPADA, have much smaller  $H_2/N_2$  and  $O_2/N_2$  permselectivity coefficients compared with those polyimides without flexible segments. Except for 6FDA-MDA and BPADA-MDA, the permeability coefficients of MDA-based polyimides of  $H_2$ ,  $O_2$ , and  $N_2$  are larger than those of ODA-based ones.

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