Permeability and permselectivity of gases in fluorinated and non-fluorinated polyimides

Kazuhiro Tanaka, Hidetoshi Kita, Masaaki Okano and Ken-ichi Okamoto*
Department of Advanced Materials Science and Engineering, Faculty of Engineering,
Yamaguchi University, Ube, Yamaguchi, 755 Japan

Solubility and permeability coefficients for gases in a series of fluorinated and non-fluorinated polyimides were measured to investigate the effects of chemical structure on permeability and permselectivity. Polyimides with higher concentration of fluorine had lower chain packing density and higher permeability. Polyimides with $-C(CF_3)_2-$ linkages had higher permeability with relatively higher permselectivity. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/2,2-bis(4-aminophenyl)hexafluoropropane (6FDA-BAHF) polyimide with two $-C(CF_3)_2-$ linkages in the polymer repeat unit displayed excellent performance for CO_2/CH_4 and O_2/N_2 separations; its permeabilities for O_2 and CO_2 were 3.7 and 3.1 times, respectively, larger than those of 6FDA-pp'ODA (4,4'-oxydianiline), a conventional 6FDA-based polyimide, while the permselectivities for O_2/N_2 and CO_2/CH_4 were 13% and 22%, respectively, smaller. On the other hand, polyimides having two $-C(CF_3)_2-$ linkages together with two ether ones in the repeat unit had lower permeability with a similar level of permselectivity as compared with 6FDA-BAHF polyimide. For H_2/CH_4 and H_2/CO separations, polyimides prepared from 6FDA and meta-oriented non-fluorinated diamines were preferable. These separation properties were discussed in connection with packing density and local segmental mobility.

(Keywords: gas separation; polyimide; fluorine; permeability; diffusion coefficient; solubility coefficient)

INTRODUCTION

Application of polyimides as gas separation membranes has become of great interest because of their excellent thermal, chemical and mechanical properties. We have reported the influences of aggregation structure induced by thermal treatment and of chemical structure of diamine moieties on gas permeability and permselectivity for polyimides based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)[1,2]. We have also reported the effect of copolymerization of para- and meta-oriented diamines on gas transport properties[3]. Kim et al. and Stern et al. have reported that some polyimides prepared from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and/or fluorine-containing diamines have high permeability[4-6].

In this study, gas solubility and permeability coefficients for a series of fluorinated and non-fluorinated polyimides prepared from four kinds of tetracarboxylic dianhydrides and six kinds of diamines were measured to investigate the effects of chemical structure on gas permeability and permselectivity.

EXPERIMENTAL

Four tetracarboxylic dianhydrides were used in this study, namely pyromellitic dianhydride (PMDA), BPDA, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 6FDA. The six diamines used are 2,2-bis-(4-aminophenyl)hexafluoropropane (BAHF), 2,2-bis(4-

(4-aminophenoxy)phenyl)hexafluoropropane (BAPHF), 2,2-bis(4-(4-amino-2-trifluoromethylphenoxy)phenyl)-hexafluoropropane (BATPHF), 4,4'-oxydianiline (pp'ODA), 3,4'-oxydianiline (mp'ODA) and 2-(3-amino-phenyl)-2-(4-aminophenyl)propane (APAP).

Poly(amic acids) were prepared at a concentration of 15–20 wt% solids by the slow addition of a stoichiometric amount of the dianhydride to a mechanically stirred solution of the diamine in N,N-dimethylacetamide (DMAc) under a nitrogen atmosphere at room temperature. Polymerization solutions were stirred for 3–12 h. For PMDA-, BPDA- and BTDA-based polyimides, the poly(amic acid) solutions thus prepared were filtered, cast onto glass plates at 80°C using a doctor blade, and then dried at 80°C for 2 h. The poly(amic acid) films were taken off the glass plates in water and dried at 65°C for 2 h in vacuum, and thermally imidized at 200°C for 20 h in vacuum. For 6FDA-based poly-imides, the poly(amic acid) solutions were diluted with DMAc to 5 wt% and chemically imidized by addition of a mixture of acetic anhydride and triethylamine (four-fold molar quantity to base unit of the poly(amic acid)). After stirring at room temperature for 1 h and then at 50°C for another 1 h, the reaction solutions were poured into methanol. The polyimide solids precipitated were washed with methanol several times, and then dried. The 15 wt% DMAc solutions of polyimides were filtered, cast onto glass plates at 80°C using a doctor blade, and dried at 80°C for 2 h. The polyimide films were taken off the glass plates in water and dried at 65°C for 2 h and finally dried at 200°C for 20 h.

* To whom correspondence should be addressed

The chemical structures of polyimides prepared are shown in *Figure 1*. Characterization of the films was carried out by methods described elsewhere[1]. The vacuum time-lag method[1] was used to measure permeability coefficient P. A dual-volume type sorption cell[7] was used to measure solubility coefficient S. The P and S values were measured at 10 atm and 35°C for H_2, CO_2, CO, N_2 and CH_4 gases and at 2 atm for O_2 and N_2. Average diffusion coefficient $\bar{D}$ was evaluated by the equation $\bar{D} = P/S$. Infra-red spectra of the films were measured with a Shimazu FTIR-4200 spectrophotometer.

The precision in the sorption measurement was estimated to be $\pm 3 \times 10^{-4}$ cm^3(STP) cm^{-3} cmHg^{-1} from the blank experiments. This corresponded to $\pm 30\%$ of the solubility coefficient of H_2 (S_{H_2}) in magnitude and

General Structure

PMDA   BPDA   BTDA   6FDA

pp'-ODA   mp'-ODA   APAP   BAHF

BAPHF   BATPHF

Figure 1 Chemical structures of polyimides used in this study

therefore it was impossible to discuss the values of S_{H_2} in detail. The precision in P was estimated to be within $\pm 3\%$.

RESULTS AND DISCUSSION

Characterization

Characterization results for the polyimides are listed in *Table 1*. Fraction of 'free space' V_F refers to the ratio of the so-called 'expansion volume'[8] to the observed volume and was calculated from the following equation:

$$V_F = (V_T - V_0)/V_T$$

where V_T is the specific molar volume at temperature T and V_0 is the volume occupied by the molecules at 0 K per mole of repeat unit of the polymer. V_0 was estimated to be 1.3 times[9] the van der Waals volume calculated by the group contribution method reported by Bondi[10]. Solubility parameter δ was calculated by the group contribution method reported by van Krevelen[11]. The concentrations of fluorine, carbonyl group and ether group in polyimides are also listed in *Table 1*. The wide-angle X-ray diffraction curves of all polyimide films were broad and structureless, indicating that they were amorphous.

The imidization step was monitored by infra-red spectroscopy. For thermal imidization, BTDA–BAPHF poly(amic acid) films of 20 and 5–10 μm thickness were heated at 200°C for 10 h, and then for another 10 h and finally at 300°C for 1 h. The absorption bands near 3200 cm^{-1} (O–H stretch) and 3350 cm^{-1} (N–H stretch), which appeared strongly for the original poly(amic acid) films, disappeared for all the heated films. The intensities of the imide absorptions near 1780 cm^{-1} (symmetrical C=O stretch) and 1380 cm^{-1} (C–N stretch) normalized against the internal aromatic absorption near 1500 cm^{-1}
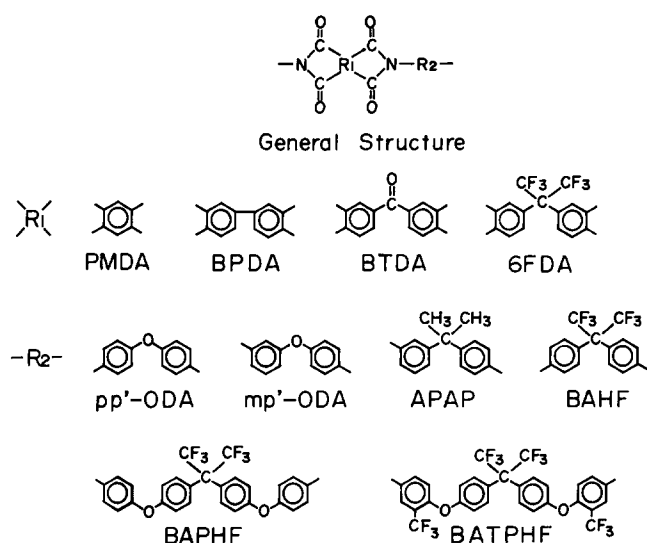
Table 1 Characterization of polyimide films[a]

Polyimide	Code no.	$[\eta]$ (dl g^{-1})	T_g (°C)	Density (g cm^{-3})	V_F	δ (J$^{1/2}$ cm$^{-3/2}$)	Concentration (10^{-3} mol cm^{-3})		
							F	–CO–	–O–
PMDA–mp'ODA	1F	1.21	–	1.406	0.122	34.6	0	14.7	3.7
PMDA–pp'ODA	1D	2.63	(420)	1.395	0.129	34.6	0	14.6	3.6
PMDA–BAPHF	1A	0.99	302	1.408	0.165	26.9	12	8.0	4.0
PMDA–BATPHF	1O	0.48	253	1.474	0.182	24.7	21	7.0	3.5
PMDA–BAHF	1B	0.74	(380)	1.478	0.158	27.7	17	11.4	0
BPDA–pp'ODA	2D	–	270	1.366	0.121	32.3	0	11.9	3.0
BPDA–BAPHF	2A	1.79	244	1.387	0.158	26.6	11	7.1	3.6
BPDA–BATPHF	2O	0.53	223	1.443	0.177	24.7	19	6.3	3.2
BPDA–BAHF	2B	0.77	329	1.424	0.157	27.2	14	9.6	0
BTDA–pp'ODA	3D	1.77	266	1.374	0.124	32.7	0	14.1	2.8
BTDA–BAPHF	3A	1.54	232	1.384	0.163	27.0	10	8.6	3.4
BTDA–BATPHF	3O	0.73	220	1.457	0.170	25.2	19	7.7	3.1
BTDA–BAHF	3B	0.59	298	1.437	0.153	27.7	14	11.6	0
6FDA–mp'ODA	4F	0.46	260	1.438	0.162	27.2	14	9.5	2.4
6FDA–APAP	4G	0.70	260	1.361	0.163	25.8	13	8.6	2.1
6FDA–pp'ODA	4D	2.04	299	1.432	0.165	27.2	14	9.4	2.4
6FDA–BAPHF	4A	0.54	243	1.429	0.181	24.3	19	6.2	3.1
6FDA–BATPHF	4O	0.71	234	1.484	0.190	23.0	25	5.6	2.8
6FDA–BAHF	4B	0.95	305	1.480	0.182	24.1	24	8.0	0

[a] $[\eta]$ is inherent viscosity at 0.5 wt% and 35°C of polyimides for 6FDA-based polyimides and of poly(amic acids) for other polyimides in DMAc solution
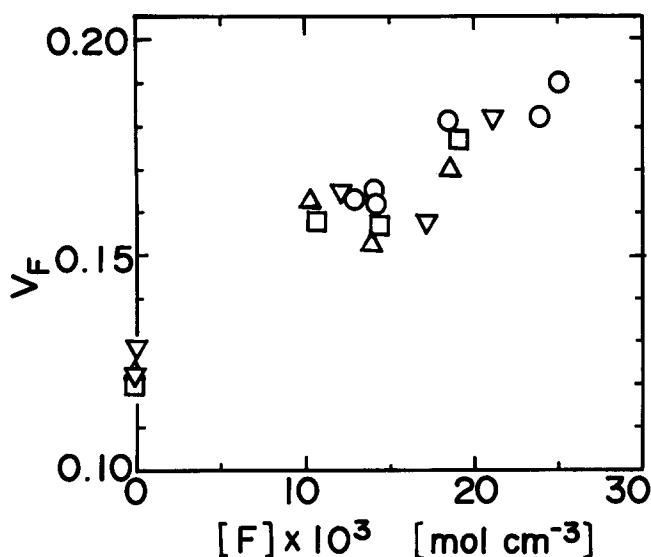
Figure 2 Relation between fraction of free space and concentration of fluorine: (∇) PMDA-based polyimides; ($\square$) BPDA-based polyimides; ($\triangle$) BTDA-based polyimides; ($\bigcirc$) 6FDA-based polyimides

have been used for determination of the degree of imidization[12]. The measurements were done for the 5–10 μm thick films. The intensity of the 1780 cm^{-1} band increased from 0.015 for the non-heated films to 0.20 for the films heated at 200°C for 20 h. Similarly, the intensity of the 1380 cm^{-1} band increased from 0.06 to 0.50. However, there was no clear difference in the normalized intensities among the three types of heated films. These results indicated that heat treatment at 200°C for 20 h was adequate for complete imidization. In the case of the other polyimides imidized thermally or chemically, disappearance of the 3200 and 3350 cm^{-1} bands was checked for the films used for the permeation measurements.

The polyimides with higher concentration of fluorine had lower values of δ, indicating that introduction of fluorine reduced molecular interaction of polymer segments. As shown in *Figure 2*, the polyimides with higher concentration of fluorine had higher values of V_F. Both reduced molecular interaction and a steric effect induced by CF_3 groups appear to disturb efficient packing of polymer chains, resulting in an increase in V_F. The polyimides prepared from *mp'*ODA had lower values of V_F than those from *pp'*ODA. It is considered that the larger degree of conformational freedom of a *meta*-oriented main chain as compared to that of a *para*-oriented one permits more efficient packing of the polymer chain in forming films[13]. This may also explain why BPDA- and BTDA-based polyimides had a somewhat smaller V_F than PMDA-based polyimides prepared from the same diamine.

PMDA-based polyimides had much higher glass transition temperatures T_g than the other polyimides from the corresponding diamines because of rigidity of the PMDA moiety. 6FDA-based polyimides had higher T_g than BPDA- and BTDA-based polyimides, because of the restricted torsional motion of phenyl rings around a –C(CF_3)$_2$– linkage[4,14]. The T_g of polyimides also depended on the diamine moieties in the order BAHF > *pp'*ODA > *mp'*ODA $\simeq$ APAP > BAPHF > BATPHF. The restricted torsional motion around a –C(CF_3)$_2$– linkage caused the higher T_g for BAHF than for *pp'*ODA.

The polyimides from BAPHF and BATPHF had a lower T_g because of the higher concentrations of ether linkages. The torsional motion of phenyl rings linked via the *meta*-position is considered to be restricted because such motion requires the cooperative motion of adjacent moieties. However, the polyimides prepared from *mp'*ODA had lower T_g than those from *pp'*ODA. This is probably because of higher configurational entropy due to a larger degree of conformational freedom of the *meta*-oriented polymer chain[3]. Changing the diamine from BAPHF to BATPHF resulted in reductions in T_g. The increase in conformation freedom caused by introduction of CF_3 groups onto the asymmetric position tends to decrease T_g, while steric restriction of motion of phenyl rings caused by the side groups tends to increase T_g. The present result indicates that the former effect is predominant.

Permeability and permselectivity

Figures 3a–d show the plots of P ratios *versus* P of the higher permeative gas for H_2/CH_4, H_2/CO, CO_2/CH_4 and O_2/N_2 systems. Permeation data were not obtained for PMDA–BAHF polyimide, because the films were not tough enough to withstand measurements at 10 atm. The values of P and P ratios for H_2/CH_4 and CO_2/CH_4 systems in 6FDA–ODA, 6FDA–BAPHF and PMDA–BAPHF were in agreement with those reported by Stern *et al.*[6]. On the other hand, P_{CO_2} in PMDA–ODA in this study was three times larger than that reported by Stern *et al.*[6]. This seems to be due to some difference in morphology of PMDA–ODA polyimide films caused by the different conditions of imidization[15,16]. For every system, there was a general trend that the polyimides having higher P had lower P ratio. The decrease in P ratio with increasing P was larger for H_2/CH_4 and H_2/CO systems with large difference in size of gas molecules than for O_2/N_2 system with relatively small difference in size. The decrease in P_{CO_2}/P_{CH_4} with increasing P_{CO_2} was rather small.

The permeation and separation properties for H_2/CH_4, H_2/CO, CO_2/CH_4 and O_2/N_2 systems are listed in *Tables 2–4*. They are discussed in terms of solubility and diffusion coefficients in the following sections.

Solubility and solubility selectivity

The S values for more condensable gases in these polyimides were larger. The logarithms of S for gases in each polyimide increased almost linearly with increasing Lennard–Jones force constants of gases in a similar manner as reported in organic solvents and rubbery polymers[17,18].

The polyimides with higher V_F tended to have larger S. The polyimides with higher concentrations of carbonyl groups also tended to have larger S for CO_2, indicating the presence of interaction between CO_2 and carbonyl groups to some extent. The value of S varied by up to 2.5 times among the polyimides investigated in this study. *Figure 4* shows plots of S ratios for O_2/N_2 and CO_2/CH_4 systems *versus* concentrations of carbonyl groups. The solubility ratios of O_2/N_2 were almost constant in the range from 1.3 to 1.5. Although the solubility ratios of CO_2/CH_4 tended to increase with increase in the concentration of carbonyl groups, the variation was within 35% and was much less than the large variation with similar change in concentration of carbonyl groups reported by Koros[19].
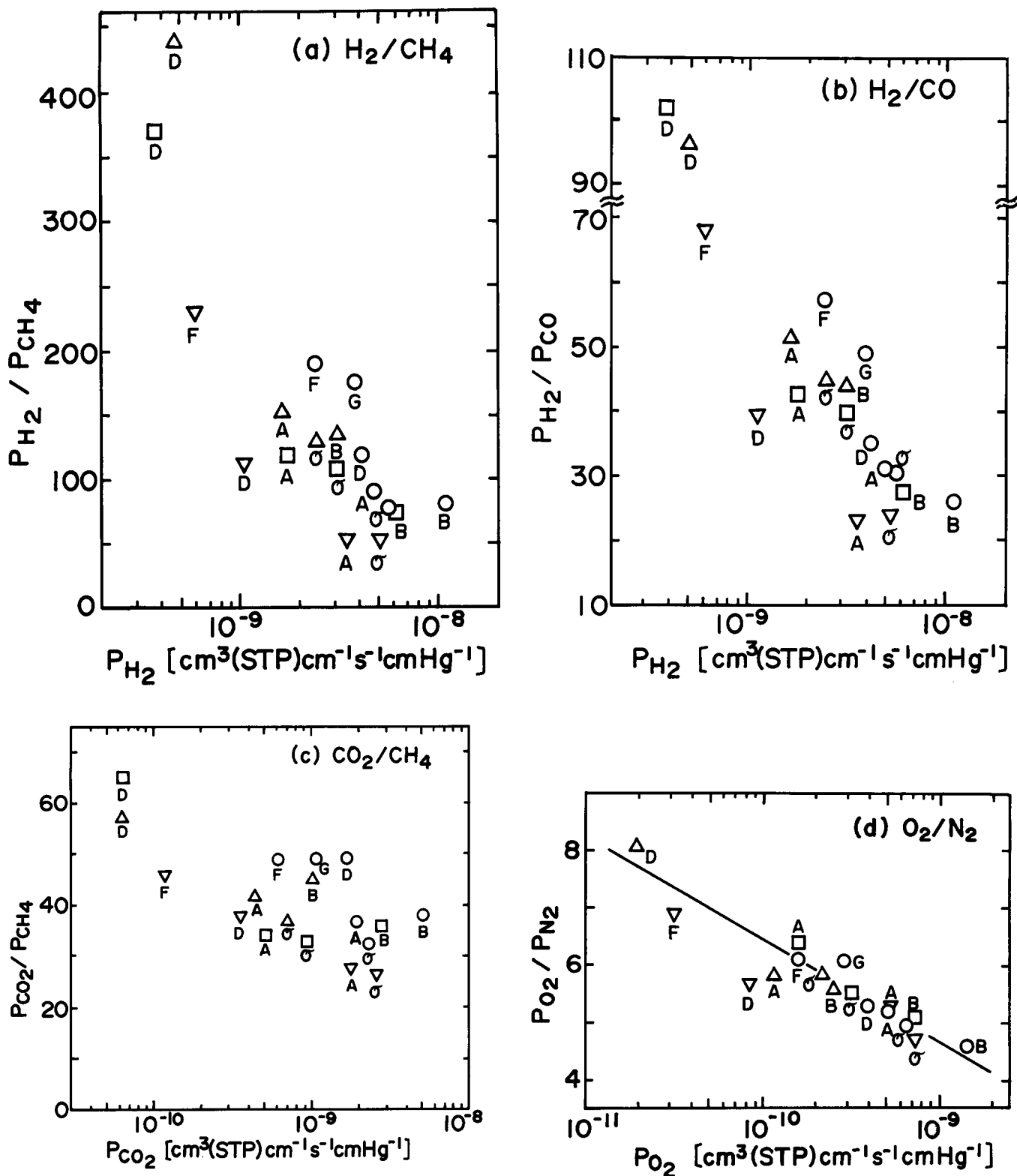
Figure 3 Plots of P ratios *versus* P of permeative gas at 35°C and 10 atm for H_2/CH_4, H_2/CO and CO_2/CH_4 systems and at 2 atm for O_2/N_2 system. The symbols are as in *Table 1* and *Figure 2*

Diffusivity and diffusivity selectivity

The factors controlling diffusion coefficient and diffusivity selectivity for glassy polymers are considered to be the packing density and the local mobility of polymer chains. The V_F is a measure of the average packing density. Generally, with increasing V_F, the diffusion coefficient of a penetrant increases, while diffusivity selectivity, which depends on the difference in size and shape of the penetrants, decreases. As for the polymer

matrix with similar packing density, higher local segmental mobility can momentarily create holes large enough, at a higher rate, for a large penetrant molecule to pass through. This results in a lower diffusivity selectivity compared with the polymer chains with lower local segmental mobility.

Figure 5 shows the plots of log $\bar{D}$ for CO_2 *versus* V_F^{-1} in polyimides investigated in this study together with the data for other glassy polymers summarized in the

Table 2 Permeability, diffusion and solubility coefficients and permeability coefficient ratios for H_2/CO and H_2/CH_4 systems in polyimides at 35°C and 10 atm[a]

Polyimide	P_{H_2}	$\bar{D}_{H_2}$	S_{H_2}	P_{CO}	$\bar{D}_{CO}$	S_{CO}	P_{H_2}/P_{CO}	P_{H_2}/P_{CH_4}
PMDA–mp'ODA	5.92	2.7	2.2	0.0866	0.14	6.2	68	229
PMDA–pp'ODA	10.6	7.9	1.4	0.270	0.42	6.5	39	110
PMDA–BAPHF	34.3	22	1.5	1.48	2.4	6.3	23	54
PMDA–BATPHF	50.4	22	2.3	2.10	2.7	7.7	24	54
BPDA–pp'ODA	3.68	–	–	0.036	–	–	100	370
BPDA–BAPHF	17.3	5.8	3.0	0.405	0.59	6.8	43	120
BPDA–BATPHF	30.6	10	3.0	0.768	1.1	7.3	40	110
BPDA–BAHF	59.1	40	1.5	2.16	2.3	9.3	27	76
BTDA–pp'ODA	4.79	3.6	1.3	0.0499	0.11	4.5	96	440
BTDA–BAPHF	16.1	11	1.5	0.313	0.58	5.4	51	150
BTDA–BATPHF	24.6	8.4	2.9	0.549	0.76	7.2	45	130
BTDA–BAHF	30.8	6.7	4.6	0.699	0.58	12	44	140
6FDA–mp'ODA	23.7	15	1.6	0.414	0.55	7.5	57	190
6FDA–APAP	38.2	22	1.7	0.776	0.93	8.4	49	180
6FDA–pp'ODA	40.7	24	1.7	1.16	1.4	8.1	35	120
6FDA–BAPHF	47.4	46	1.0	1.51	2.3	6.5	31	91
6FDA–BATPHF	55.4	12	4.6	1.82	1.9	9.4	30	79
6FDA–BAHF	108	29	3.7	4.14	3.4	12	26	81

[a] P is in 10^{-10} cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹. $\bar{D}_{H_2}$ is in 10^{-7} cm² s⁻¹ and $\bar{D}_{CO}$ is in 10^{-8} cm² s⁻¹. S is in 10^{-3} cm³(STP) cm⁻³ cmHg⁻¹

Table 3 Permeability, diffusion and solubility coefficients and the ratios of each coefficient for CO_2/CH_4 system in polyimides at 35°C and 10 atm[a]

Polyimide	P_{CO_2}	$\bar{D}_{CO_2}$	S_{CO_2}	P_{CH_4}	$\bar{D}_{CH_4}$	S_{CH_4}	P_{CO_2}/P_{CH_4}	$\bar{D}_{CO_2}/\bar{D}_{CH_4}$	S_{CO_2}/S_{CH_4}
PMDA–mp'ODA	1.18	0.28	42	0.0258	0.023	11	46	12	3.8
PMDA–pp'ODA	3.55	0.80	45	0.0937	0.079	12	38	10	3.8
PMDA–BAPHF	17.6	4.1	43	0.638	0.51	13	28	8.1	3.4
PMDA–BATPHF	24.6	5.3	47	0.937	0.69	14	26	7.7	3.4
BPDA–pp'ODA	0.642	0.18	36	0.0099	0.011	9.5	65	16	3.8
BPDA–BAPHF	4.96	1.4	35	0.145	0.12	12	34	12	3.0
BPDA–BATPHF	9.15	2.4	39	0.279	0.23	12	33	10	3.2
BPDA–BAHF	27.7	4.6	60	0.780	0.44	18	36	11	3.4
BTDA–pp'ODA	0.625	0.19	32	0.0109	0.013	8.5	57	15	3.8
BTDA–BAPHF	4.37	1.2	36	0.105	0.10	10	42	12	3.5
BTDA–BATPHF	6.94	1.8	38	0.189	0.16	12	37	12	3.2
BTDA–BAHF	10.1	1.7	59	0.226	0.12	19	45	14	3.1
6FDA–mp'ODA	6.11	1.3	46	0.125	0.092	14	49	14	3.4
6FDA–APAP	10.7	2.2	49	0.217	0.14	16	49	16	3.1
6FDA–pp'ODA	16.7	3.1	54	0.341	0.22	16	49	14	3.4
6FDA–BAPHF	19.1	4.2	45	0.520	0.40	13	37	11	3.4
6FDA–BATPHF	22.8	5.7	40	0.703	0.49	14	32	12	2.8
6FDA–BAHF	51.2	8.1	63	1.34	0.66	20	38	12	3.1

[a] P is in 10^{-10} cm³(STP) cm⁻¹ s⁻¹ cmHg⁻¹. $\bar{D}$ is in 10^{-8} cm² s⁻¹. S is in 10^{-3} cm³(STP) cm⁻³ cmHg⁻¹

previous paper[20]. The polymers with higher V_F tended to have higher $\bar{D}_{CO_2}$. The relationship between V_F and $\bar{D}$ for other gases was similar to that for CO_2. The $\bar{D}_{CO_2}$ varied by a factor of 45 among the polyimides investigated here. The variation in P was mainly due to that in $\bar{D}$. The reductions in $\bar{D}$ on changing the diamine from pp'ODA to mp'ODA were larger than those predicted from the small decreases in V_F. This is considered to be due to the lower local segmental mobility of meta-linked polymer chains compared to para-linked ones. The phenylene rings connected to adjacent moieties at a

para-position can rotate even though the neighbouring moieties are fixed. However, the phenylene ring connected at a meta-position cannot rotate without cooperative motion of the neighbouring moieties. In a solid state, the local mobility of a meta-linked phenylene ring is restricted. This is consistent with the view suggested by Pavlova et al. on calculating conformational parameters; that is, the rotation about a bond passing through a ring is forbidden if this virtual bond and valence bonds joined to the ring do not lie on a straight line[21].

Figure 6 shows the plots of $\bar{D}$ ratios of CO_2 to CH_4

Table 4 Permeability, diffusion and solubility coefficients and the ratios of each coefficient for O_2/N_2 system in polyimides at 35°C and 2 atm[a]

Polyimide	P_{O_2}	$\bar{D}_{O_2}$	S_{O_2}	P_{N_2}	$\bar{D}_{N_2}$	S_{N_2}	P_{O_2}/P_{N_2}	$\bar{D}_{O_2}/D_{N_2}$	S_{O_2}/S_{N_2}
PMDA–mp'ODA	0.31	0.47	6.6	0.0454	0.097	4.7	6.9	5.5	1.3
PMDA–pp'ODA	0.825	1.0	8.1	0.145	0.32	4.5	5.7	4.4	1.3
PMDA–BAPHF	4.98	6.7	7.4	0.943	2.1	4.6	5.3	3.8	1.4
PMDA–BATPHF	7.06	7.8	9.0	1.50	2.5	6.1	4.7	3.5	1.3
BPDA–BAPHF	1.54	2.0	7.6	0.245	0.44	5.5	6.3	5.0	1.3
BPDA–BATPHF	3.11	4.0	7.7	0.563	0.93	6.0	5.5	4.4	1.3
BPDA–BAHF	7.1	6.6	11	1.39	2.0	6.8	5.1	3.9	1.3
BTDA–pp'ODA	0.191	0.42	4.5	0.0236	0.077	3.1	8.1	5.8	1.4
BTDA–BAPHF	1.14	1.9	6.0	0.195	0.49	3.9	5.9	4.4	1.3
BTDA–BATPHF	2.17	2.7	8.1	0.370	0.63	5.9	5.9	4.6	1.3
BTDA–BAHF	2.50	1.9	13	0.45	0.47	9.6	5.6	4.6	1.2
6FDA–mp'ODA	1.57	1.9	8.4	0.259	0.45	5.8	6.1	4.7	1.3
6FDA–APAP	2.89	3.0	9.7	0.473	0.78	6.1	6.1	4.5	1.4
6FDA–pp'ODA	3.88	3.4	12	0.733	1.1	6.6	5.3	4.0	1.3
6FDA–BAPHF	5.13	6.0	8.5	0.981	2.0	4.8	5.2	3.6	1.5
6FDA–BATPHF	6.50	6.1	11	1.30	1.6	8.0	5.0	4.2	1.2
6FDA–BAHF	14.2	10	14	3.11	2.8	9.9	4.6	3.7	1.2

[a] P is in $10^{-10}\,cm^3(STP)\,cm^{-1}\,s^{-1}\,cmHg^{-1}$. $\bar{D}$ is in $10^{-8}\,cm^2\,s^{-1}$. S is in $10^{-3}\,cm^3(STP)\,cm^{-3}\,cmHg^{-1}$
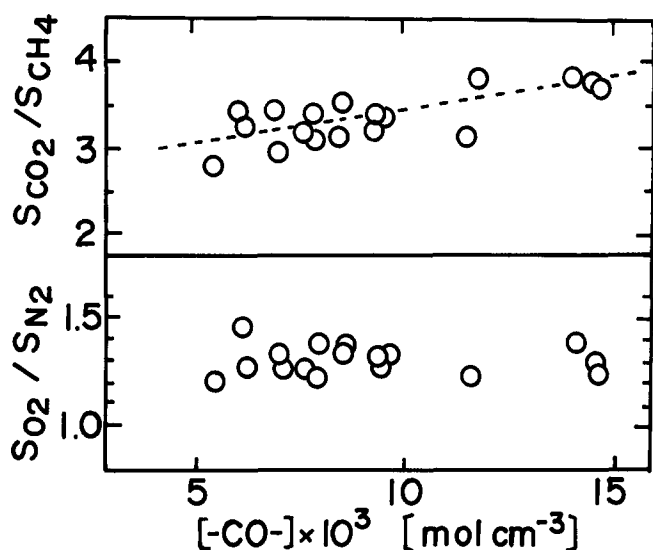
Figure 4 Plots of S ratios for O_2/N_2 and CO_2/CH_4 systems at 35°C *versus* concentration of carbonyl groups

Figure 5 Plots of $\log \bar{D}_{CO_2}$ at 35°C and 10 atm *versus* V_F^{-1}: (O) polyimides used in this study; (□) data for glassy polymers summarized in Table 4 in ref. 20

and of O_2 to N_2 *versus* V_F^{-1}. For the CO_2/CH_4 system, the $\bar{D}$ ratios depend significantly on the kind of acid dianhydride moieties; that is, they were in the order 6FDA > BPDA $\simeq$ BTDA > PMDA. It is supposed that the rigid and plane structure of PMDA moiety inhibits uniform packing of the polymer chains and introduce voids large enough for large penetrant molecules to pass through, resulting in lower $\bar{D}$ ratios for PMDA-based polyimides than for other polyimides. It has been pointed out that the torsional motion of phenyl rings around a $-C(CF_3)_2-$ linkage is restricted, and that the mobility of phenyl rings around an ether linkage is relatively high[4,14]. These are also obvious from molecular model examination using a Stuart-type model. The higher $\bar{D}$ ratios for 6FDA-based polyimides is attributed to lower
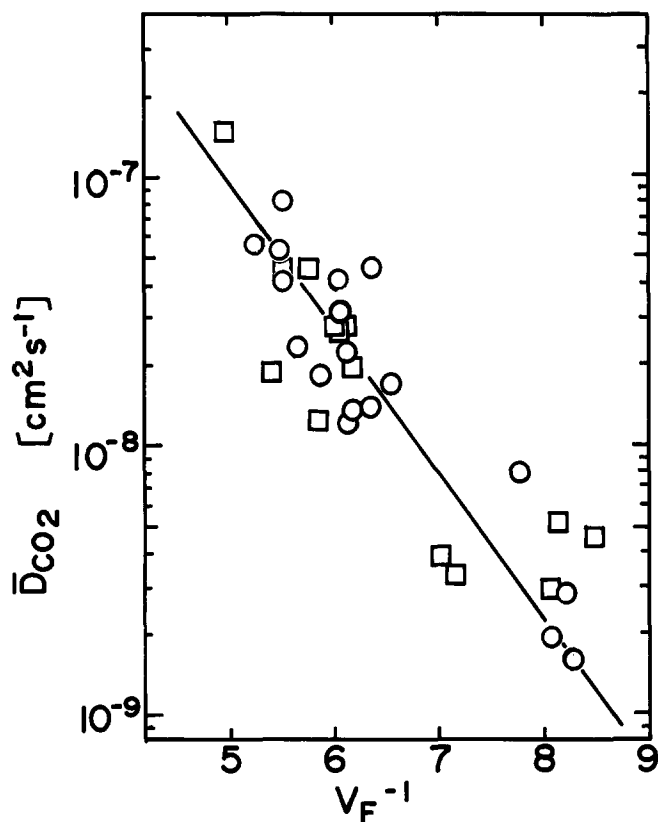
local segmental mobility of the acid dianhydride moieties and to lower concentration of ether linkages in the polymer, as compared with BPDA- and BTDA-based polyimides. For the O_2/N_2 system, the differences in $\bar{D}$ ratios among the different acid dianhydrides were not distinct. As O_2 and N_2 molecules are similar in both size
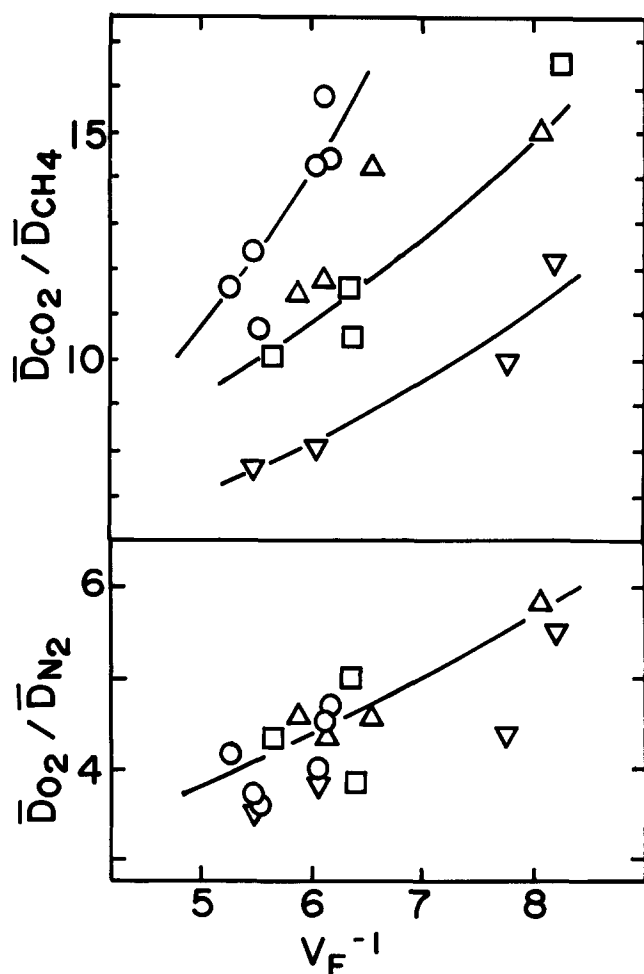
Figure 6 Plots of $\bar{D}$ ratios for CO_2/CH_4 and O_2/N_2 at 35°C *versus* V_F^{-1}. The symbols are as in *Figure 2*

and shape, the effects of changes in V_F and in local segmental mobility on $\bar{D}$ seem similar for both gases.

CO_2/CH_4 separation

As can be seen from *Figure 3c*, the polyimides from 6FDA and/or BAHF exhibited higher values of P_{CO_2} together with higher values of P_{CO_2}/P_{CH_4}. The reason seems to be that the lower segmental mobility around a $-C(CF_3)_2-$ linkage acts as a factor to increase the $\bar{D}$ ratio as described above and compensates loss of the $\bar{D}$ ratio with an increase in V_F. 6FDA–BAHF polyimide with two $-C(CF_3)_2-$ linkages in the basic unit had the highest value of P_{CO_2} among the polyimides investigated in this study together with a relatively high value of P_{CO_2}/P_{CH_4}. Introduction of $-C(CF_3)_2-$ linkages into the polymer chains is very effective in improving permeability and permselectivity for CO_2/CH_4 separation.

The polyimides from BAPHF had much lower values of P_{CO_2} together with slightly lower values of P_{CO_2}/P_{CH_4} as compared with the polyimides from BAHF, although there is no significant differences in V_F between these two kinds of polyimides. This seems to be attributed to the high concentration of ether linkages in the former.

Changing the diamine from BAPHF to BATPHF resulted in small increases in P_{CO_2} and small decreases in P_{CO_2}/P_{CH_4}. Additional introduction of CF_3 side groups into the polyimides having $-C(CF_3)_2-$ linkages in the main chains showed a rather small effect on the permeability because of additional small increases in V_F.

Molecular model examination suggested that the side groups reduced the torsional mobility of phenyl rings to some extent. However, this steric effect did not appreciably act as a factor to increase diffusivity selectivity or permselectivity.

H_2/CH_4 and H_2/CO separations

As can be seen from *Figures 3a* and *3b*, *P* ratios for H_2/CH_4 and H_2/CO systems decrease rapidly with increasing P_{H_2} in contrast to the CO_2/CH_4 system. The increases in P_{H_2} with introduction of fluorine were smaller than those in P_{CO_2}, while the decreases in P_{H_2}/P_{CH_4} and P_{H_2}/P_{CO} are much larger than those in P_{CO_2}/P_{CH_4}. It is considered that the diffusivity selectivities for gas pairs with large differences in molecular size are influenced mainly by packing density of polymer segments and that the contribution of local segmental mobility to the diffusivity selectivity is rather small. Consequently, introduction of $-C(CF_3)_2-$ linkages or CF_3 groups significantly decreases the diffusivity selectivity and *P* ratios, and was not very effective for these gas separations. The polyimides with moderately high packing density and low local mobility such as 6FDA–APAP and 6FDA–*mp'*ODA were favourable for H_2/CH_4 or H_2/CO separations.

O_2/N_2 separation

As can be seen from *Figure 3d*, the plots of P_{O_2}/P_{N_2} *versus* P_{O_2} in polyimides investigated here fall approximately on a line, in contrast to those for other gas separations. This is attributed to the fact that the effects of chemical structure on diffusion coefficients are similar for both O_2 and N_2 gases because of similarity of their molecular size and shape, as described above.

Decreases in P_{O_2}/P_{N_2} with increasing P_{O_2} were relatively small. As the result of increases in P_{O_2}, introduction of $-C(CF_3)_2-$ linkages or CF_3 groups was very effective for O_2/N_2 gas separation.

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