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Correlation between Positron Annihilation and Gas Diffusion Properties of a Series of Polyimides

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The lifetime and the intensity of ortho-positronium (*o*-Ps), τ_3 and I_3, respectively, were measured for a series of polyimides prepared from 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]diphthalic dianhydride. Average size of free space holes probed by *o*-Ps, $v_{h,Ps}$, was evaluated from τ_3 using an empirical equation. There was a clear correlation between logarithm of diffusion coefficients, $\overline{D}$, of CO_2 and CH_4 and $v_{h,Ps}$ for the polyimides. Large differences in $\overline{D}$ among the polyimides having the same fractional free space, V_F, were attributed to differences in $v_{h,Ps}$. There was a fairly good correlation between log $\overline{D}$ and $(v_{h,Ps}I_3)^{-1}$, suggesting that I_3 is a measure of the concentration of free space holes which can accommodate *o*-Ps, at least for the polyimides with the similar chemical structure. Correlation between V_F and $v_{h,Ps}I_3$ was rather poor.

Polyimides are thermally and chemically stable and have good mechanical properties. The relationships between chemical structure and gas permeation properties of polyimides have been investigated by changing their chemical structure systematically.[1-6] Factors controlling the average diffusion coefficient $\overline{D}$ of a penetrant in glassy polymers are considered to be packing density and local mobility of the polymer chains. Volume fraction of "free-space"[7] is usually used as a measure of the average packing density of the polymer chains.[3-5] The volume fraction of free space, V_F, used in this study refers to the ratio of the so-called "expansion volume"[8] to the observed volume and was calculated from the following equation.

$$V_F=(V_T-V_0)/V_T \tag{1}$$

where V_T is the specific molar volume of repeat unit of the polymer at temperature T and V_0 is the volume occupied by the molecules at 0 K per mole of the repeat unit. V_0 was estimated to be 1.3 times[9] the van der Waals volume calculated by the group contribution method of Bondi.[10]

Gas diffusion in glassy polymers has been successfully explained on the basis of the free volume model[11] developed originally for rubbery polymers.[3,5,12]

$$D=A_dRT\exp(-B_d/V_F) \tag{2}$$

where R is the gas constant and A_d and B_d are the parameters dependent on penetrant molecular size and shape. However, some polyimides display about 7 times larger $\overline{D}$ as compared with the polyimides with similar V_F as shown in Fig. 1.[13] The diffusion coefficients are supposed to be controlled not only by the fraction of free space but also by both size of free space holes and its distribution.[3,5,13] However, this has not yet been confirmed experimentally.

Position annihilation (PA) has been applied to investigate microstructure of polymers.[14-19] PA lifetime spectra of polymers have a long-lived component which is attributed to ortho-positronium (*o*-Ps) formed and annihilated in amorphous regions. The lifetime of the long-lived

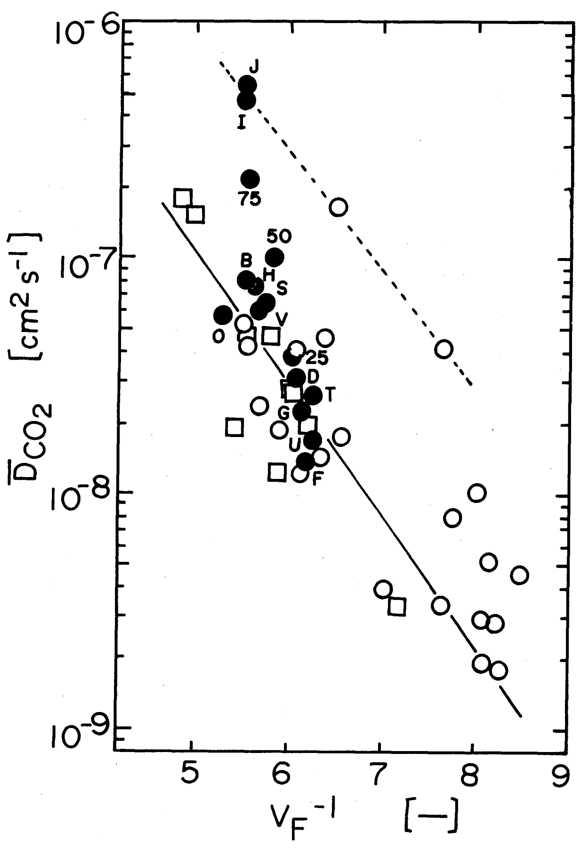

Fig. 1. Plots of log $\overline{D}_{CO_2}$ at 35 °C and 10 atm versus V_F^{-1}. The symbols are the same as in Table 1.

component, τ_3, is considered to be a good measure of the size of the microvacancy where an *o*-Ps is trapped and annihilated by a pick-off annihilation rate depending on the size of the microvacancy. The intensity of the long-lived component, I_3, is sometimes considered to be a measure of the number of such vacancies. However, our recent study on *o*-Ps formation in various polyimides indicated that sufficient care should be taken in correlating I_3 with the number of the microvacancies because Ps intensity can be affected by inhibition and quenching effects.[20)]

It is not clear how closely the microvacancies probed by *o*-Ps are related to the free space holes which concern gas diffusion in amorphous glassy polymer films. It is, therefore, interesting to investigate the PA properties of the polyimides mentioned above and to correlate them to the diffusion properties. In this paper, we report on our study of correlations, for which there have been only a few reports for glassy polymers.[21,22)]

Experimental

4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]diphthalic acid (6FDA)-based polyimides, whose chamical structure is shown in Fig. 2, were used in this study. Their preparation and characterization were described elsewhere.[5,13)] The data of average diffusion coefficients of CO_2 and CH_4, $\bar{D}_{CO_2}$ and $\bar{D}_{CH_4}$ respectively, in these polyimides were cited from Refs. 5 and 13, and are listed in Table 1. All the PA lifetime measurements were carried out at the Inter-University Laboratory for the Common Use of JAERI facilities.[23)] The positron source was about 25 μCi of ^{22}NaCl sandwiched between thin nickel foils (2.8 mg cm^{-2} thick and 0.5×0.5 cm^2 wide). Sample films (1×1 cm^2 wide and 20 to 100 μm thick) were stacked to make 1 mm thickness, and two equivalent stacks were placed in a

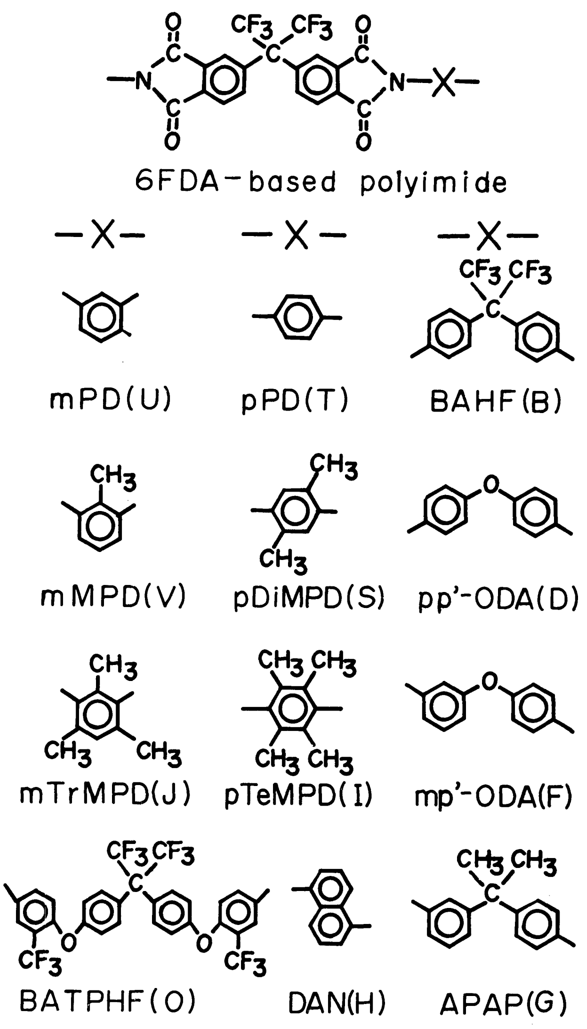

Fig. 2. Chemical structure of the polyimides used.

Table 1. Physical Properties of Polymers Used in This Study

Code No.	Polymer	T_g	Density	V_F	$\bar{D}_{CO_2}$	$\bar{D}_{CH_4}$
		°C	g cm^{-3}	[−]	10^{-8} cm^2 s^{-1}	10^{-8} cm^2 s^{-1}
4B	6FDA-BAHF	305	1.480	0.182	8.1	0.66
4D	-*pp*′ODA	299	1.432	0.165	3.1	0.22
4F	-*mp*′ODA	260	1.438	0.162	1.3	0.092
4G	-APAP	260	1.361	0.163	2.2	0.14
4H	-DAN	383	1.422	0.178	7.7	0.52
4I	-*p*TeMPD	420	1.330	0.182	48	9.6
4J	-*m*TrMPD	377	1.352	0.182	54	9.9
4O	-BATPHF	234	1.484	0.190	5.7	0.49
4S	-*p*DiMPD	355	1.390	0.175	6.5	0.48
4T	-*p*PD	351	1.473	0.161	2.6	0.16
4U	-*m*PD	298	1.474	0.160	1.7	0.099
4V	-*m*MPD	335	1.416	0.176	6.2	0.42
4IU(75)[a)]		386	1.355	0.180	22	3.0
4IU(50)[a)]		355	1.395	0.172	10	1.1
4IU(25)[a)]		323	1.433	0.166	3.9	0.34
PBMA		34	1.051	0.164		
PSt		104	1.045	0.180		
PC		149	1.200	0.166		

a) Copolyimides from 6FDA with *p*TeMPD and *m*PD. The number in parentheses refers to feed ratio (mol%) of *p*TeMPD.

glass tube together with the positron source in the sandwich geometry. The sample tube was evacuated and the PA lifetime was measured at a room temperature (297 K). The PA lifetime spectrometer was the fast-fast coincidence equipment with the time resolution of 0.30 ns (FWHM).[23] Each PA lifetime spectrum, having more than one million total count, was analyzed into three lifetime components using the computer program PATFIT.[24]

Results and Discussion

A typical lifetime spectrum of PA is shown in Fig. 3. The first two components, with lifetimes and corresponding intensities τ_1=0.1—0.2 ns, I_1=19—32% and τ_2=0.43—0.49 ns, I_2=53—62% are attributed to self annihilation of para-positroniums and direct annihilation of positrons. Only the data of the long lifetime component are listed in Table 2.

PA spectroscopy sometimes provides a useful technique for surface characterization.[25] It is probable that surface layer of a film acts as traps of positrons and positroniums and influences attempts to measure the bulk properties of the film. It is, therefore, customary to use samples having enough thickness to minimize the surface effect. In the present study, relatively thin films (20 to 100 μm thick) had to be used for the PA measurements in order to ensure the same sample conditions as used for sorption and permeation measurements. Therefore, it was first checked if the surface layer effect could be neglected for such thin films. Table 3 shows the effect of film thickness on PA lifetime and intensity for five different polymers. For poly(butyl methacrylate) (PBMA),[26] polystyrene (PSt),[19] and bisphenol-A polycarbonate (PC)[18] there were no substantial differences in τ_3 and I_3 between 2—3 mm thick films and less than 100 μm thick ones, taking the differences in sample sources and preparation methods into account. For the polyimides, τ_3 was the same between thick and thin films within experimental errors, but I_3 was a little larger for thin films. If the effect of the surface layer on *o*-Ps formation were present, it should affect not only I_3 but also τ_3; τ_3 should become much larger. This was not the present case. A slight increase in I_3 for the thin films may be due to some small difference in the microstructure of the films. We concluded anyway that the PA data obtained in this study reflect the bulk properties of the films.

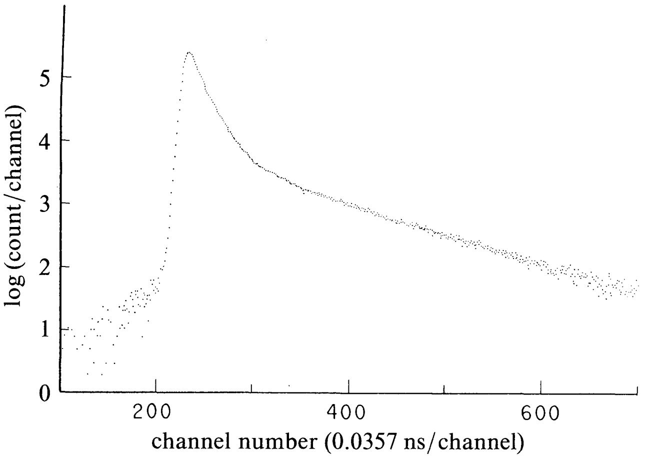

Fig. 3. Typical PA lifetime spectrum for 6FDA-*p*PD polyimide (after background subtraction).

Table 2. PA Properties of Polymers Used in This Study

Polymers	τ_3	I_3	R	$v_{\mathrm{h,Ps}}$	$v_{\mathrm{h,Ps}}I_3$
	ns	%	nm	nm^3	nm^3%
4B	2.98	17.1	0.362	0.198	3.39
4D	2.40	9.37	0.319	0.136	1.27
4F	2.40	7.72	0.319	0.136	1.05
4G	2.47	12.7	0.325	0.143	1.82
4H	2.84	9.62	0.352	0.183	1.76
4I	3.94	17.6	0.420	0.310	5.46
4J	3.63	15.9	0.403	0.273	4.33
4O	2.68	16.5	0.340	0.165	2.72
4S	3.15	14.3	0.373	0.217	3.10
4T	2.72	10.9	0.343	0.169	1.84
4U	2.57	7.88	0.332	0.153	1.21
4V	2.80	11.3	0.349	0.178	2.01
4IU(75)	3.32	15.5	0.384	0.236	3.66
4IU(50)	3.15	15.2	0.373	0.217	3.29
4IU(25)	2.71	11.1	0.343	0.168	1.86
PBMA	2.34	29.1	0.314	0.130	3.79
PSt	2.10	35.1	0.294	0.106	3.72
PC	2.07	29.0	0.291	0.103	2.99

Table 3. Effect of Sample Thickness on PA Properties

Polymers	Thickness	τ_3	I_3	$\tau_3 I_3$
	μm	ns	%	ns %
4H	60	2.87	8.83	25.3
	25	2.81	9.74	27.4
	25	2.86	9.49	27.1
4J	133	3.61	13.8	49.8
	30	3.62	15.8	57.2
	30	3.64	15.9	57.9
PBMA	2000	2.16	28	60
	100	2.34	29.1	68.1
PSt	3200	2.05	33.0	67.7
	36	2.10	35.1	73.7
PC	3000	2.12	29.0	61.5
	55	2.07	29.0	60.0

Figure 4 shows plots of I_3 vs. τ_3. The 6FDA-based polyimides having larger τ_3 trend to show larger I_3. It is noted that the 6FDA-based polyimides show larger τ_3 and smaller I_3 as compared with the glassy non-imide polymers including the ones reported previously.[27]

By assuming a simple quantum mechanical model where a positronium resides in an infinite spherical potential of radius R_0 with an electron layer of thickness ΔR, the following correlation between τ_3 and average radius R (=R_0−ΔR) of microvacancies has been obtained.[28,29]

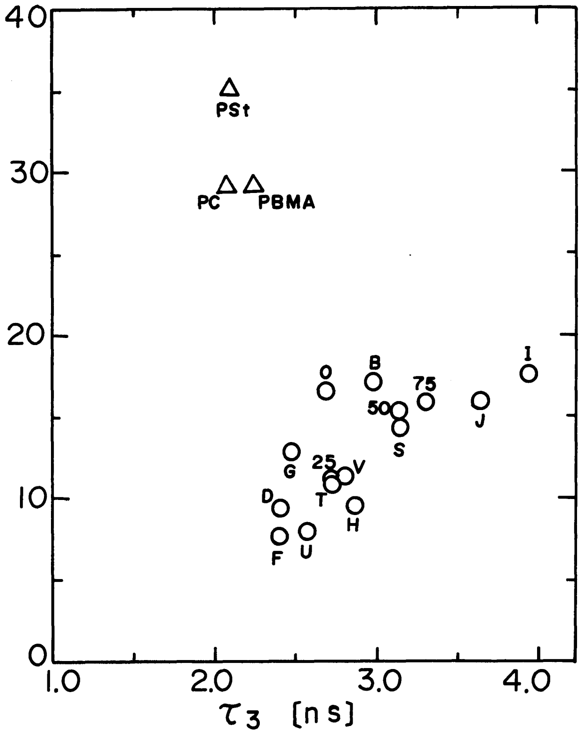

Fig. 4. Plots of I_3 versus τ_3 for 6FDA-based polyimides and three glassy non-imide polymers. The symbols are the same as in Table 1.

$$\tau_3^{-1} = 2[1-(R/R_0)+(1/2\pi)\sin(2\Delta R/R_0)],\ (\mathrm{ns}^{-1}) \qquad (3)$$
$$R_0 = R + \Delta R,\ \Delta R = 0.166\ \mathrm{nm}.$$

Average volume of microvacancies seen by *o*-Ps, $v_{\mathrm{h,Ps}} = (4/3)\pi R^3$, was calculated from Eq. 3 and is also listed in Table 2. The R for the 6FDA-based polyimides investigated varies from 0.319 nm ($v_{\mathrm{h,Ps}}$=0.136 nm^3) for 4*D* to 0.420 nm ($v_{\mathrm{h,Ps}}$=0.310 nm^3) for 4*I*. The R values are fairly larger than those for glassy non-imide polymers such as poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (0.26 nm),[15], polystyrene(0.294 nm), polycarbonate(0.291 nm), PBMA(0.314 nm).

There is an argument whether microvacancies probed by *o*-Ps are pre-exsisting interstitial spaces among the frozen polymer chains or bubbles formed around Ps. Kobayashi et al. have recently reported that Ps bubbles are formed in glassy polymers as in liquids.[30] On the other hand, we claimed the former case, judging from the effects of vapor sorption on τ_3 and I_3 for 6FDA-*m*TrMPD polyimide.[31] The above-mentioned fact that the polyimides with much higher glass transition temperatures (T_g) show larger τ_3 than the glassy polymers with much lower T_g also strongly suggests the former case. Microvacancies probed by *o*-Ps are considered to be pre-exsisting interstitial spaces among the frozen polymer chains, and are hereafter referred to as "free space holes" probed by *o*-Ps.

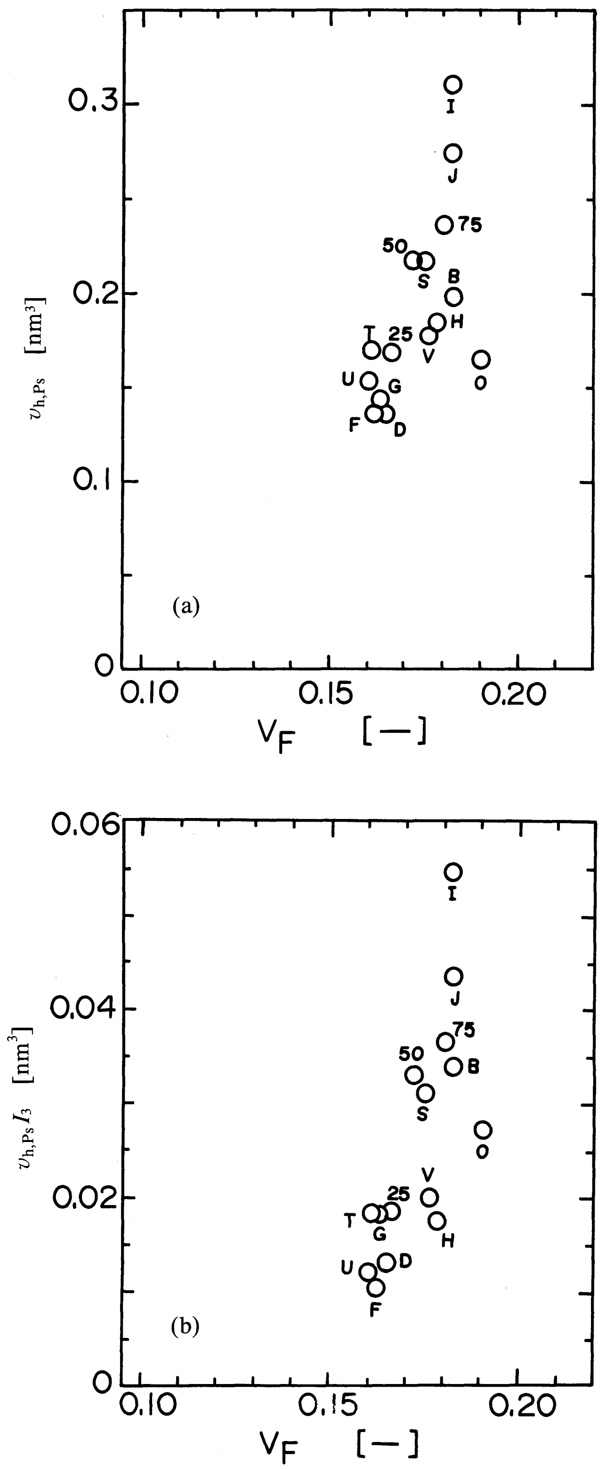

Fig. 5. Plots of $v_{\mathrm{h,Ps}}$ (a) and $v_{\mathrm{h,Ps}}I_3$ (b) versus V_F for 6FDA-based polyimides. The symbols are the same as in Table 1.

Figures 5(a) and (b) show plots of $v_{\mathrm{h,Ps}}$ and $v_{\mathrm{h,Ps}}I_3$, respectively, versus V_F. Although there is a very rough trend that the polymers with larger V_F have lareger $v_{\mathrm{h,Ps}}$ and $v_{\mathrm{h,Ps}}I_3$, the data points scatter significantly.

Figures 6 and 7 show plots of log $\overline{D}$ of CO_2 and CH_4 versus $v_{\mathrm{h,Ps}}$ and I_3, respectively, for the 6FDA-based

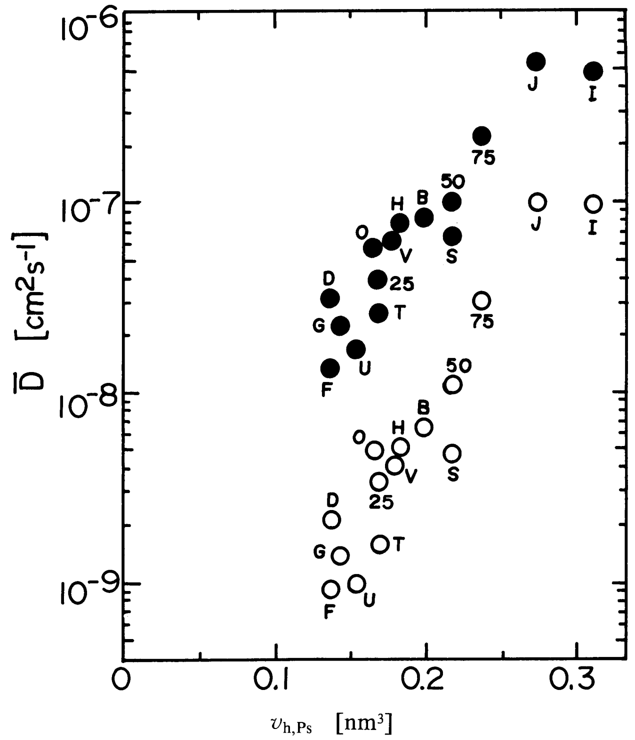

Fig. 6. Plots of log $\overline{D}$ of CO_2 (●) and CH_4 (○) versus $v_{\mathrm{h,Ps}}$ for 6FDA-based polyimides. The symbols are the same as in Table 1.

polyimides. There are a clear correlation between log $\overline{D}$ and $v_{\mathrm{h,Ps}}$ and a rough correlation between log $\overline{D}$ and I_3.

We will compare 6FDA-*p*TeMPD, -*m*TrMPD and -BAHF polyimides having the same value of V_F (see Fig. 2 as to their chemical structure). The values of $\overline{D}_{\mathrm{CO_2}}$ and $\overline{D}_{\mathrm{CH_4}}$ are 6—7 and 15 times, respectively, larger for 6FDA-*p*TeMPD and -*m*TrMPD polyimides than for 6FDA-BAHF. The values of $v_{\mathrm{h,Ps}}$ are 57% and 38% larger for 6FDA-*p*TeMPD and -*m*TrMPD, respectively than for 6FDA-BAHF. The differences in I_3 among these polyimides are rather small. The much larger values of D for the former two polyimides are thus ascribed to the larger values of $v_{\mathrm{h,Ps}}$. This may be explained by considering the distribution of the volume fraction of free space as illustrated in Fig. 8. We consider two different polymers having the same V_F but different distribution, namely, average volume of free space holes is larger for polymer-1 than for polymer-2. The total area under the distribution curve expresses V_F. Only the free space holes large enough for a penetrant molecule to pass through can contribute to the diffusion of the penetrant in a glassy polymer. The effective diameters for diffusion of CO_2 and CH_4 are 0.35 nm and 0.38 nm, respectively. Therefore, free space holes larger than v_h=0.022 and 0.029 nm³ can contribute to the diffusion of CO_2 and CH_4, respectively. The volume fraction of such free space holes, $V_{\mathrm{F,dif}}$ is expressed as the area of the part larger than the critical volume of diffusion under the distribution curve. Polymer-1 has larger $V_{\mathrm{F,dif}}$ than polymer-2 and consequently has larger $\overline{D}$. Free space holes larger than v_h=0.033 nm³ (R=0.2 nm) can accommodate *o*-Ps. The higher is the fraction of the holes with larger v_h among such free space holes, the

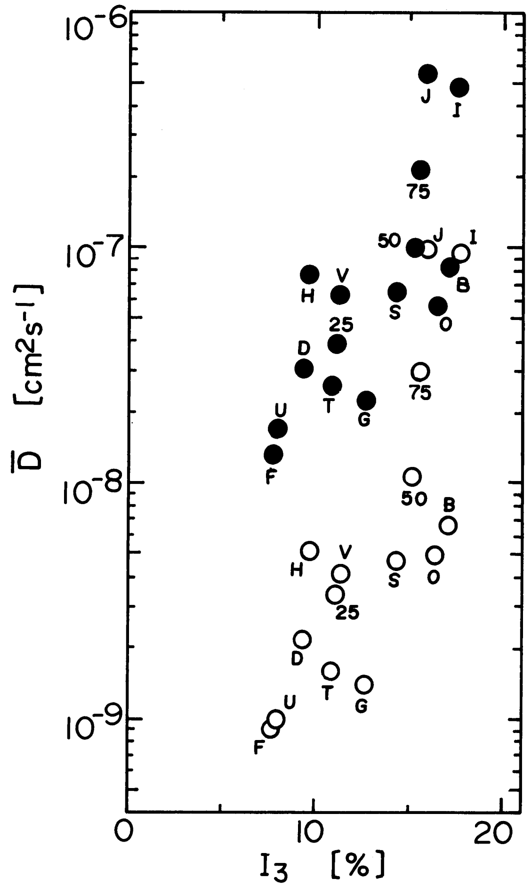

Fig. 7. Plots of log $\overline{D}$ of CO_2 (●) and CH_4 (○) versus I_3 for 6FDA-based polyimides. The symbols are the same as in Table 1.

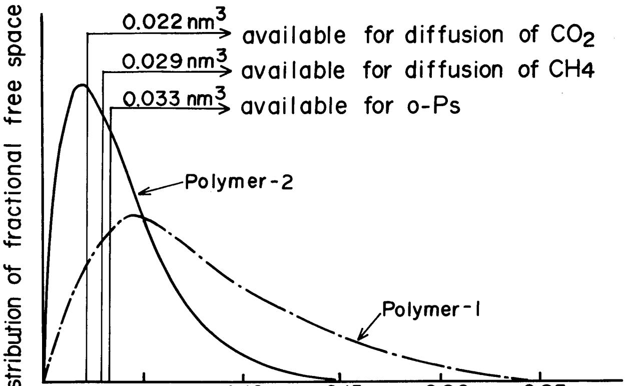

Fig. 8. Model of distribution of free space holes and relation between the free space holes available for penetrants and *o*-Ps.

larger is the $v_{h,Ps}$. As a result, $v_{h,Ps}$ is larger for polymer-1.

For several glassy polymers, Volkov et al. have reported that there is a correlation between log D and $(\tau_3)^{-1}$ but there is no correlation between log D and $(\tau_3 I_3)^{-1}$.[21,32] Kobayashi et al. have also reported a correlation between log D and τ_3.[30] The clear correlation between log $\overline{D}$ and $v_{h,Ps}$ observed for 6FDA-based polyimides in the present study was also the case for other polyimides.[27] In general, weak molecular interaction, bulky substituents and twisted structure are apt to cause less-efficient packing of the polymer chains and result in large free space holes. Therefore, it is natural that the polymers with larger $v_{h,Ps}$ have larger $\overline{D}$. However, the fact that log $\overline{D}$ is better correlated with $v_{h,Ps}$ than with V_F^{-1} may imply a presence of a more direct and intrinsic relationship between $v_{h,Ps}$ and $\overline{D}$.

Volume fraction of free space holes probed by o-Ps, $V_{F,Ps}$, is given by the product of $v_{h,Ps}$ and concentration of free space holes which can accommodate o-Ps, $C_{h,Ps}$. For some polymers, I_3 has been considered to be proportional to $C_{h,Ps}$.[14-16] For 6FDA-based polyimides I_3 was roughly correlated with τ_3 and log $\overline{D}$. Although it is not clear whether I_3 is a measure of $C_{h,Ps}$ for the 6FDA-based polyimides, $v_{h,Ps}I_3$ was tentatively used as a measure of $V_{F,Ps}$ in this study. Figure 9 shows plots of log $\overline{D}$ versus $(v_{h,Ps}I_3)^{-1}$ for the 6FDA-based polyimides. There is a fairly good correlation between log $\overline{D}$ and $(v_{h,Ps}I_3)^{-1}$. This means that I_3 can be used as a measure of $C_{h,Ps}$ at least for a series of polymers having the similar chemical structure. The fact that $\overline{D}$ is correlated more closely to $v_{h,Ps}I_3$ and therefore to $V_{F,Ps}$ than to V_F is understood based on that the volume fraction of free space holes available for the diffusion, $V_{F,dif}$, is much closer to $V_{F,Ps}$ than to V_F, as can be seen in Fig. 8. As mentioned above, the correlation of V_F with $v_{h,Ps}$ or $v_{h,Ps}I_3$ is rather poor. This is because the size distribution of free space holes differ from one polymer to another.

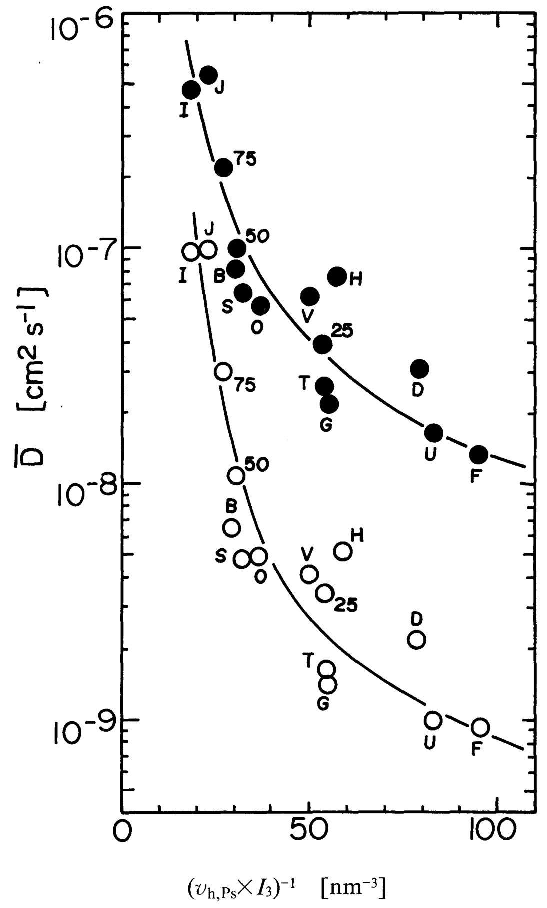

Fig. 9. Plots of log $\overline{D}$ of CO_2 (●) and CH_4 (○) versus $(v_{h,Ps}I_3)^{-1}$ for 6FDA-based polyimides. The symbols are the same as in Table 1.

Conclusion

Microvacancies probed by o-Ps in 6FDA-based polyimides are considered to be pre-exsisting interstitial spaces among the frozen polymer chains rather than Ps bubbles. Diffusion of penetrants in glassy polymers is considered to be primarily controlled by volume fraction of free space holes large enough for the penetrant molecules to pass through rather than by volume fraction of whole free space holes, V_F. Therefore, it is reasonable that diffusion coefficients of CO_2 and CH_4 in the 6FDA-based polyimides were correlated much better with a measure of volume fraction of free space holes probed by o-Ps, $v_{h,Ps}I_3$, than with V_F. A clear correlation between average volume of free space holes probed by o-Ps, $v_{h,Ps}$ and diffusion coefficients was also observed. The clear reason are now under investigation.

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