Correlation between Positron Annihilation and Sorption of CO₂ in Glassy Polymers

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ABSTRACT: The lifetime and the intensity of *ortho*-positronium (*o*-Ps), τ_3 and I_3 respectively, were measured for polyimides and non-imide polymers in glassy state. Average size of free space holes probed by *o*-Ps, $v_{h,Ps}$ is calculated from τ_3 using an empirical equation. Correlations between sorption of CO₂ and the positron annihilation (PA) properties are discussed. The Langmuir capacity constant C'_H of the dual-mode sorption model is well correlated with $v_{h,Ps}$, suggesting that the larger $v_{h,Ps}$, reflects the higher volume fraction of holes large enough to be available for the Langmuir type sorption. The Henry's law solubility constant k_D is also correlated with $v_{h,Ps}$, indicating that the polymers packed less-efficiently tend to have larger k_D . As a result, there is a tendency that solubility coefficient of CO₂ at 10 atm, S_{CO_2} , increases with $v_{h,Ps}$. The C'_H , k_D , and S_{CO_2} are also correlated with $v_{h,Ps}I_3$ for only the polyimides, and the correlations are a little worse than those with $v_{h,Ps}$.

KEY WORDS Positron Annihilation / CO₂ Sorption / Dual-Mode Sorption Model / Polyimides / *ortho*-Positronium / Free Space Hole / Glassy Polymers / Solubility Coefficient /

Polyimides have attracted much attention for their use in gas separation membranes. In previous papers,^{1,2} we investigated relations between CO₂ sorption properties and other properties of polyimides. The sorption isotherms were well described by the dual-mode sorption model. Langmuir affinity constant b increased with an increase in the content of functional groups [FG] such as carbonyl and sulfonyl groups. Henry's law solubility constant k_D increased with an increase in a composite parameter reflecting magnitude of both [FG] and fraction of free space V_F . Langmuir capacity constant C'_H increased with an increase in glass transition temperature T_g , but the correlation line between C'_H and T_g for nonfluorinated polyimides was different from

that for other glassy polymers including fluorinated polyimides. There was a tendency that solubility coefficients of CO₂ in glassy polymers at 10 atm increase with increasing T_g . This was because proportion of the Langmuir component in the total sorption at 10 atm was about two-thirds for the polymers investigated.

Positron annihilation (PA) has been applied to investigate microstructure in polymers.³⁻⁵ 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 component, τ_3 , is considered to be a good measure of the size of the microvacancies where *o*-Ps is trapped. The intensity of the component, I_3 is sometimes considered

to be a measure of the number of such microvacancies.

We have recently reported that diffusion coefficients of CO₂ and CH₄ in the polyimides prepared from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) are well correlated with the average size of microvacancies evaluated from τ_3 .^{6,7} The microvacancies probed by *o*-Ps were considered to be pre-existing interstitial spaces among the polymer chains, and were referred to as "free space holes" probed by *o*-Ps.⁷ It is also interesting to investigate correlations between the PA and CO₂ sorption properties of the polyimides. In this paper, we report on such correlations for a series of polyimides prepared from 6FDA and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) together with other glassy polymers.

EXPERIMENTAL

Chemical structure of the 6FDA- and BPDA-based polyimides, other polyimides and polybenzoxazole (FPBO-1) are shown in Figure 1. Preparation and characterization of the polyimides and FPBO-1 were described elsewhere.^{1,2,8-12} Polysulfone (PSF) and polycarbonate (PC) films were supplied from Nissan Chemical Industries Ltd. and Mitsubishi Gas Chemical Co., Ltd., respectively. Polystyrene (PS) ($M_w = 505000$) prepared by suspension polymerization was supplied from Sekisui Plastics Co., Ltd. in powder form. PS films were prepared by casting its benzene solution onto glass plates and then by drying at 70°C for 2 hours. CO₂ sorption data for the polyimides and FPBO-1 were cited from ref 1, 2, 8-13. The data for PSF, PC, and PS were cited from ref 14, 15, and 16, respectively.

All the PA lifetime measurements were carried out at the Inter-University Laboratory for the Common Use of JAERI facilities.¹⁷ The positron source was about 25 μ Ci of ²²NaCl sandwiched between thin nickel foils (2.8 mg cm⁻² thick and 0.5 $\times$ 0.5 cm² wide). Sample

Figure 1. Chemical structure of polyimides and polybenzoxazole.

films (1 $\times$ 1 cm² wide and 20 to 30 μ m thick) were stacked to make 1 mm thickness, and two equivalent stacks were placed in a 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 (24°C). The PA lifetime spectrometer was the fast-fast coincidence equipment with the time resolution of 0.30 ns (FWHM).¹⁷ Each PA lifetime spectrum, having more than one million total counts, was analyzed into three lifetime components using the computer program PATFIT.¹⁸

RESULTS AND DISCUSSION

$$V_F = (V_T - V_0)/V_T \quad (1)$$

Characterization results and solubility coefficients of CO₂, S_{CO_2} , at 35°C and 10 atm for the polymers are listed in Table I. All of the polymers investigated were amorphous judging from wide angle X-ray diffraction spectra. Solubility coefficient S was obtained by dividing amount of gas sorbed C by equilibrium pressure p ; $S = C/p$. Fraction of "free space" V_F was calculated by

where V_T is the molar volume per 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 times¹⁹ the van der Waals volume calculated by the group contribution method of Bondi.²⁰

According to the dual-mode sorption model,^{21,22} equilibrium concentration C of a

Table I. Physical properties of the polymers^a

Code No.	Polymers	T_g °C	Density g cm ⁻³	V_F g cm ⁻³	S_{CO_2}
Polyimides					
4I	6FDA-pTeMPD	420	1.330	0.182	92
4J	-mTrMPD	377	1.352	0.182	80
4S	-pDiMPD	355	1.390	0.175	66
4V	-mMPD	335	1.416	0.176	65
4H	-DAN	383	1.422	0.178	64
4B	-BAHF	305	1.480	0.182	63
4T	-pPD	351	1.473	0.161	59
4U	-mPD	298	1.474	0.160	55
4D	-pp'ODA	299	1.432	0.165	54
4G	-APAP	260	1.361	0.163	49
4F	-mp'ODA	260	1.438	0.162	46
4O	-BATPHF	234	1.484	0.190	40
4IU (75)		386	1.355	0.180	77
4IU (50)		355	1.395	0.172	81
4IU (25)		323	1.433	0.166	63
2J	BPDA-mTrMPD	385	1.241	0.155	84
2W	-DDBT	> 490	1.372	0.125	61
2B	-BAHF	329	1.424	0.157	60
2E	-DDS	350	1.410	0.118	54
2BC		295	1.365	0.172	52
2O	-BATPHF	223	1.443	0.177	39
2D	-ODA	270	1.366	0.121	36
2A	-BATHF	244	1.387	0.158	35
2G	-APAP	279	1.274	0.131	35
5D	TCDA-ODA	350	1.357	0.124	59
PEI		215	1.285	0.143	30
Non-imide polymers					
FPBO-I		290	1.461	0.207	53
PSF		186	1.237	0.162	30
PC		145	1.200	0.166	26
PS		100	1.045	0.174	15

^a S_{CO_2} is at 35°C and 10 atm, and in $10^{-3} \text{ cm}^3(\text{STP}) \text{ cm}^{-3} \text{ cmHg}^{-1}$. 4IUs: copolyimides from 6FDA with pTeMPD and mPD. The figures in parentheses refer to feed ratio (mol%) of pTeMPD, 2BC: a copolyimide from BPDA with a mixture of BAHF and BAMHF (1/3).

Table II. Parameters of CO₂ sorption for polymers^a

Polyimides	k_D	C'_H	b
4I	2.24	70.0	0.495
4J	2.22	60.4	0.499
4S	1.40	45.5	0.636
4B	1.68	43.2	0.453
2B	1.66	39.6	0.564
4T	1.53	40.7	0.562
4D	1.34	34.0	0.516
4F	1.14	28.4	0.540
2W	1.17	39.0	0.847
2E	1.40	30	0.86
2D	0.75	23	0.55
5D	1.23	35	0.73
PEI	1.00	14	0.56
FPBO-1*	1.23	36.4	0.317
PSF	0.725	19.2	0.39
PC	0.685	18.8	0.262
PS	0.5	9	0.17

^a k_D is in cm³ (STP) cm⁻³ atm⁻¹, b is in atm⁻¹, and C'_H is in cm³ (STP) cm⁻³.

* Unpublished data.

penetrant in a glassy polymer is represented by the following equation.

$$C = k_D p + C'_H b p / (1 + b p) \quad (2)$$

where k_D is the Henry's law solubility constant, b is the Langmuir affinity constant, and C'_H is the Langmuir capacity constant. In the previous papers,^{1,2,8,9,13} sorption isotherms of CO₂ in several polyimides were measured at 35°C and up to about 25 atm, and analyzed by eq 2. The values of the model parameters for the polymers are listed in Table II.

The first two components of a lifetime spectra, with lifetimes and corresponding intensities $\tau_1 = 0.1$ to 0.2 ns, $I_1 = 19$ to 36% and $\tau_2 = 0.40$ to 0.49 ns, $I_2 = 53$ to 78%, are attributed to self annihilation of *para*-positroniums and direct annihilation of positrons, respectively.³ The data of lifetime τ_3 and intensity I_3 of the long-lived component are listed in Table III. The 6FDA- and BPDA-based polyimides and PEI have larger τ_3 and smaller I_3 as compared with the glassy non-imide polymers and TCDA-ODA poly-

Table III. PA properties of polymers used in this study

Polymers	τ_3	I_3	R	$v_{h,Ps}$	$v_{h,Ps} I_3$
	ns	%	nm	nm ³	nm ³ %
4I	3.94	17.6	0.420	0.310	5.46
4J	3.63	15.9	0.403	0.273	4.33
4S	3.15	14.3	0.373	0.217	3.10
4V	2.80	11.3	0.349	0.178	2.01
4H	2.84	9.62	0.352	0.183	1.76
4B	2.98	17.1	0.362	0.198	3.39
4T	2.72	10.9	0.343	0.169	1.84
4U	2.57	7.88	0.332	0.153	1.21
4D	2.40	9.37	0.319	0.136	1.27
4G	2.47	12.7	0.325	0.143	1.82
4F	2.40	7.72	0.319	0.136	1.05
4O	2.68	16.5	0.340	0.165	2.72
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
2J	3.16	10.0	0.374	0.218	2.18
2W	2.83	2.6	0.351	0.181	0.47
2B	2.67	11.7	0.340	0.164	1.92
2E	—	0	—	—	0
2BC	2.51	11.7	0.328	0.147	1.71
2O	2.34	6.3	0.314	0.130	0.82
2D	2.5	0.5	0.33	0.15	0.07
2A	2.09	3.0	0.293	0.105	0.32
2G	1.79	2.3	0.265	0.078	0.18
5D	1.91	20.5	0.276	0.088	1.80
PEI	1.68	7.5	0.254	0.069	0.52
FPBO-1	3.24	21.9	0.379	0.227	4.97
PSF	1.97	21.0	0.282	0.094	1.97
PC	2.07	29.0	0.291	0.103	2.99
PS	2.10	35.1	0.294	0.106	3.72

imide. BPDA-ODA polyimide slightly displayed the long-lived component of PA, but BPDA-DDS polyimide did not at all. The values of τ_3 and $v_{h,Ps}$ for BPDA-ODA polyimide are inaccurate, and seem too large judging from the correlation between diffusion coefficient of CO₂ and $v_{h,Ps}$ for a series of polyimides.^{6,7}

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 $R (= R_0 - \Delta R)$ of free space holes has been obtained.^{23,24}

Figure 2. Plots of C'_H versus $v_{h,Ps}$ for polyimides (○) and non-imide glassy polymers (Δ).

$$\tau_3^{-1} = 2[1 - (R/R_0) + (1/2\pi)\sin(2\pi R/R_0)] \quad (\text{ns}^{-1})$$

$$R_0 = R + \Delta R, \quad \Delta R = 0.166 \text{ nm} \quad (3)$$

Average volume of free space holes seen by *o*-Ps, $v_{h,Ps} = (4/3)\pi R^3$, was calculated by eq 3, and is also listed in Table III.

Figure 2 shows plots of C'_H versus $v_{h,Ps}$. There is a good correlation between C'_H and $v_{h,Ps}$ for the glassy polymers except for TCDA-ODA polyimide, FPBO-1, and PS. The correlation line goes through the zero point. The correlation is somewhat better than that between C'_H and T_g reported in the previous paper.² The values of C'_H for non-fluorinated polyimides such as PEI, BPDA-ODA, and TCDA-ODA were somewhat smaller than those predicted from the correlation between C'_H and T_g for other glassy polymers including fluorinated polyimides.² On the other hand, the correlation line between C'_H and $v_{h,Ps}$ is valid for both types of polymers.

Figure 3(a) illustrates temperature dependence of specific volume of an amorphous polymer. The specific volume of the polymer is larger in glassy state ("A") than in the

Figure 3. Schematic illustration of temperature dependence of specific volume and size distribution of volume fraction of free space holes.

hypothetical equilibrium state ("B") by unrelaxed volume. The unrelaxed volume is considered to be present in the matrix as microvoids, which act as the sites of the Langmuir type sorption. The microvoids available for the Langmuir type sorption are considered to be part of the pre-existing free space holes which correspond to the unrelaxed volume and are larger than the occupied volume of a gas molecule sorbed in the polymer. The occupied volume of a CO₂ molecule is estimated to be 0.08 nm³ by the dilation measurements.^{25,26}

Size distribution of free space holes of a polymer is illustrated in Figure 3(b). As temperature decreases, the distribution in the rubbery state shifts to the narrow and smaller-size one which is in equilibrium at each temperature. The distribution B in Figure 3(b) illustrates the distribution in the hypothetical equilibrium state at temperature T below T_g .

In the glassy state, the distribution can not change so much as in the rubbery state, because the segmental motion is frozen. Consequently, the distribution in the glassy state at temperature T , as illustrated by the distribution A , is broader and larger in size as compared with the distribution B . The polymer contains more free-space-holes being large in size in the glassy state than in the corresponding hypothetical equilibrium state. A major part of the shaded region in Figure 3(b) is considered to correspond to the microvoids available for the Langmuir type sorption. The microvoids being smaller than the occupied volume of CO_2 (0.08 nm^3) might be also available for Langmuir-like sorption followed by the corresponding volume expansion. The dilation caused by CO_2 sorption in polycarbonate was reported to agree with the prediction based on swelling due only to the Henry's law sorption species.²⁵ It was also reported for some polymers that volume change of polymer increased linearly with CO_2 pressure except for very high pressures.²⁷ These results suggest that the Langmuir-like sorption at the smaller microvoids plays only a minor role. Judging from the larger values of $v_{h,Ps}$ as compared with the occupied volume of sorbed CO_2 , the microvoids smaller than 0.08 nm^3 are likely to be a very small portion of the whole microvoids for the polymers investigated here.

The correlation between C'_H and $v_{h,Ps}$ shown in Figure 2 suggests that $v_{h,Ps}$ reflects the volume fraction of the microvoids. At present, we cannot give a clear explanation of the reason. The $v_{h,Ps}$ is an average volume of free space holes probed by o -Ps and does not directly represent the volume fraction. However, we have recently pointed out a tendency that the rubbery polymer with larger $v_{h,Ps}$ has larger volume fraction of free space holes probed by o -Ps, $V_{F,Ps}$.²⁸ It is probable that the similar tendency is valid for glassy polymers.

Figure 4 shows plots of k_D versus $v_{h,Ps}$. There is a tendency that k_D increases with $v_{h,Ps}$,

Figure 4. Plots of k_D versus $v_{h,Ps}$. The symbols are as in Figure 2.

although the k_D values for the non-polyimides are smaller as compared with polyimides having similar $v_{h,Ps}$. Henry's law sorption is not associated directly with free space holes because it is a simple dissolution in matrix as in liquids. However, solution in Henry's law mode must include a process to make the interchain space large enough to accommodate a CO_2 molecule.² k_D depends not only on the affinity between CO_2 and the polymer but also on the ease of forming such large interchain spaces. $v_{h,Ps}$ is considered to be larger in a less-efficiently packed polymer matrix. A space large enough to accommodate a CO_2 molecule is more easily formed in such a polymer matrix. This is the reason that a correlation between k_D and $v_{h,Ps}$ is observed for the polyimides. The smaller values of k_D for the non-imide polymers are attributed to the weaker affinity to CO_2 molecules because of the lower content of functional groups such as carbonyl and sulfonyl.^{1,2}

There is no correlation between b and $v_{h,Ps}$. The b depends on only affinity between CO_2 and polymer segments. It is reasonable that there is no correlation between b and $v_{h,Ps}$.

Solubility coefficient at 10 atm is often used practically in comparison of the contribution of solubility to gas permeability among

Figure 5. Plots of S_{CO_2} at 10 atm and 35°C versus $v_{\text{h,Ps}}$. The symbols are as in Figure 2.

polymers. Figure 5 shows plots of S_{CO_2} versus $v_{\text{h,Ps}}$. S_{CO_2} at 10 atm is well correlated with $v_{\text{h,Ps}}$. As reported in the previous paper,² the proportion of the Langmuir component to the total sorption at 10 atm is about two-thirds for the polyimides and other glassy polymers. The Langmuir-type sorption is almost saturated at 10 atm and therefore differences in b values of different polymers hardly affect the amount of Langmuir-type sorption. Consequently, the variation in S_{CO_2} is mainly attributed to that in C'_H . Furthermore, there is a tendency that k_D increased with $v_{\text{h,Ps}}$. These are the reasons that there is the apparent correlation between S_{CO_2} at 10 atm and $v_{\text{h,Ps}}$.

Volume fraction of free space holes probed by *o*-Ps, $V_{\text{F,Ps}}$, is given by the product of $v_{\text{h,Ps}}$ and concentration of free space holes probed by *o*-Ps, $C_{\text{h,Ps}}$. For some polymers, I_3 was considered to be proportional to $C_{\text{h,Ps}}$.^{3,4} The product of $v_{\text{h,Ps}}$ and I_3 might be a measure of $V_{\text{F,Ps}}$ for a series of polymers having similar chemical structure. There are tendencies that C'_{H} , k_{D} , and S_{CO_2} increase with $v_{\text{h,Ps}}I_3$ except for the non-imide polymers. However, they are

correlated a little worse with $v_{\text{h,Ps}}I_3$ than with $v_{\text{h,Ps}}$. The data points for the non-imide polymers are much below the correlation lines. These results suggest that I_3 is not a good measure of $C_{\text{h,Ps}}$ for different polymers. We have recently reported that there is no clear correlation between $C_{\text{h,Ps}}$ and I_3 for rubbery polymers, probably because the proportionality constant of $C_{\text{h,Ps}}$ to I_3 is different from polymer to polymer.²⁸ The similar explanation might be possible for glassy polymers.

Volkov *et al.* reported that there was a linear correlation between solubility coefficients of CO_2 and $I_2/(1-I_2)$ for several glassy polymers.²⁹ They considered that $I_2/(1-I_2)$ was proportional to the over all concentration of traps of electrons and positrons and that such type of traps were responsible for the equilibrium gas sorption in glassy polymers. However, such a correlation between S_{CO_2} and $I_2/(1-I_2)$ for the polyimides and non-imide polymers investigated here was not observed.

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