Evaluation of polymer free volume by positron annihilation and gas diffusivity measurements

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In this paper we show that there exists a linear relationship between the size of a cavity where an *ortho*-positronium (*o*-Ps) atom annihilates by the 'pick-off' mechanism and the total free volume of the molecular liquid or polymer under consideration. This relationship is used to determine the free volume of electron irradiated poly(aryl-ether-ether-ketone) (PEEK) samples and the result is compared with that obtained from gas diffusivity measurements.

(Keywords: PEEK; positron annihilation; free volume)

INTRODUCTION

Free volume has been considered as one of the most important physical parameters for characterizing various properties of polymeric materials[1–4]. In a previous paper[5], we compared the lifteime of *ortho*-positronium (*o*-Ps) atoms in various liquids and polymers with the free volume (V_f) estimated by the group-contribution method of Bondi[6]. A good correlation was found between the two parameters. An *o*-Ps is the spin-parallel bound state between a positron and an electron. It is formed when a high energy positron emitted from a radioactive source such as ^{22}Na captures a spin-parallel electron from the surrounding medium. In molecular substances *o*-Ps annihilates through a process called 'pick-off' annihilation where the positron of *o*-Ps annihilates with one of the bound electrons with opposite spin. The pick-off annihilation lifetime is determined by the overlap of the positron and electron wave functions and hence can be related to the size of a cavity where *o*-Ps is situated at the instant of annihilation.

Although it is not quite clear whether the cavity is a pre-existing free volume hole or a hole created by the *o*-Ps itself as the result of its large zero-point energy[5,7,8], the good correlation between the lifetime and the free volume may provide a new practical means for estimating the free volume contained in molecular substances. In this present paper, we show that the correlation is improved to a quantitative level by using the *o*-Ps cavity size (estimated from the lifetime through a semi-empirical equation) as a new parameter. Based on this improved correlation, free volume in a polymer is evaluated as a function of the electron irradiation dose and the result is compared with that obtained from gas diffusivity measurements.

EXPERIMENTAL

The sample chosen for the irradiation study was poly(aryl-ether-ether-ketone) (PEEK), a radiation resistant polymer with a high glass transition temperature (~140°C). Semicrystalline and amorphous samples with a thickness of 0.2 mm for positron measurements, and an amorphous sample with a thickness of 25 μm for diffusivity measurements, were kindly supplied by the Sumitomo Chemical Co. Ltd. The samples were irradiated in air with 2-MeV electrons from a Dynamitron-type accelerator at the Takasaki Radiation Chemistry Research Establishment, JAERI. The dose rate measured with cellulose triacetate (CTA) was 5 kGy s^{-1}. Because of the high dose rate, the effect of radiation-induced oxidation was insignificant.

Positron lifetime measurements were performed with the spectrometer that has been previously described[9]. Approximately 0.37 MBq (10 μCi) of ^{22}Na sealed in a thin Kapton film was used as the positron source. Samples (1 cm × 1 cm × 0.2 mm) were stacked together to make units of 2 mm thickness and the source was sandwiched between two equivalent stacks. The lifetime data were analysed into three exponential components by computer analysis. The longest-lived component, with the lifetime τ_3 and the corresponding intensity I_3, was easily attributed to the annihilation of *o*-Ps atoms. Two other components with lifetimes τ_1 and τ_2 (and corresponding intensities I_1 and I_2) were attributed to the annihilation of spin-antiparallel *para*-positronium (*p*-Ps) atoms and free positrons, respectively.

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Complementary information on the annihilation of positronium (Ps) atoms was obtained by performing Doppler broadening measurements of the annihilation radiations. Annihilation γ-rays were recorded with a high-resolution Ge detector (EG&G Ortec, GEM10175P). From each spectrum we determined a parameter called S, which is the fraction of counts in the central part of the 0.51-MeV annihilation peak to the total counts contained in the whole peak. The S-parameter serves as a good measure of the number of p-Ps atoms formed, because the p-Ps self-annihilation accompanies a very low momentum and gives a sharp annihilation peak with a large value of S.

Gas diffusivity was determined for Ar, O_2 and N_2 by measuring the time-lags through the amorphous thin film samples. A stainless steel filter holder with an effective permeation area of 11.4 mm^2 was used as the permeation cell. Pressure measurements were carried out downstream of the permeation cell by using a Baratron pressure transducer (Model 370HS) with a full-scale range of 1.33×10^3 Pa (10 torr). The permeation time-lag Θ was measured under a pressure difference of 1.01×10^5 Pa (1 atm), with the downstream pressure being effectively zero. The diffusion coefficient D was calculated from the relationship

$$D=l^2/6\Theta$$

where l is the membrane thickness.

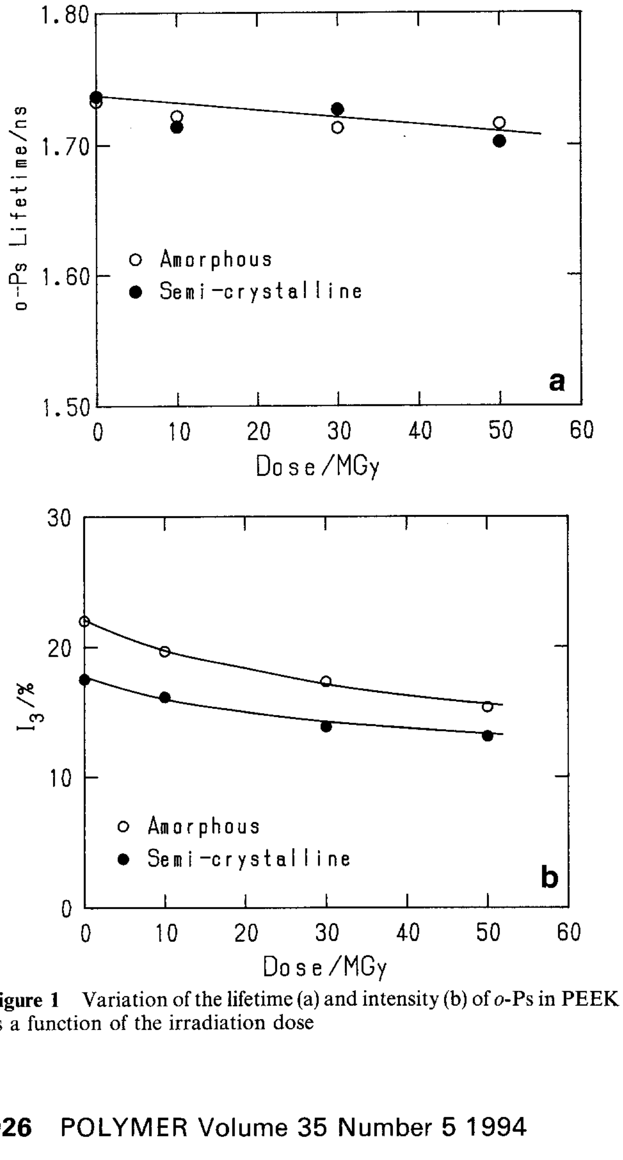

Figure 1 Variation of the lifetime (a) and intensity (b) of o-Ps in PEEK as a function of the irradiation dose

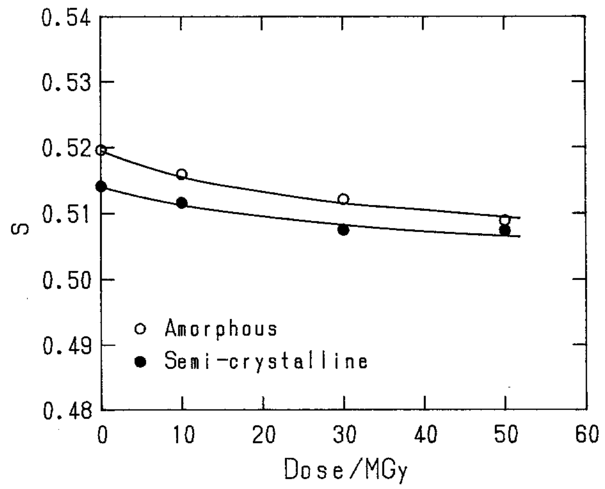

Figure 2 Variation of the S-parameter in PEEK with irradiation dose, as obtained from Doppler broadening measurements

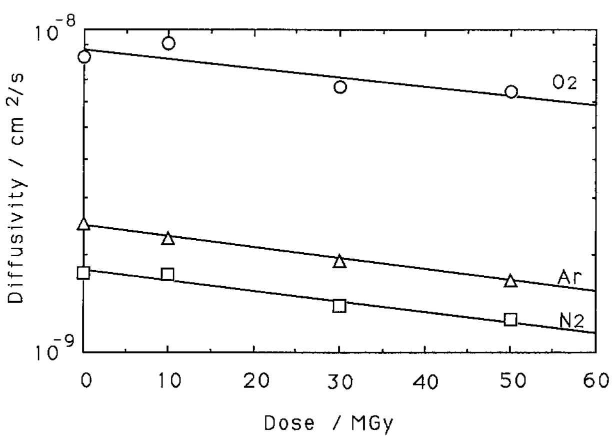

Figure 3 Variation of the diffusion coefficients of Ar, O_2 and N_2 in amorphous PEEK as a function of the irradiation dose

RESULTS

The variations of the lifetime and the intensity of the o-Ps in PEEK as a function of the irradiation dose ($\leqslant 50$ MGy) are shown in *Figure 1*, where the closed and open circles indicate the data for semicrystalline and amorphous samples, respectively. In both cases the intensity decreases markedly with irradiation dose, while the lifetime change is rather small. The results of the Doppler broadening measurements are shown in *Figure 2*. The S-parameter decreases with irradiation dose as does the o-Ps intensity (see *Figure 1b*). The effect of irradiation on the gas diffusivity is shown in *Figure 3*.

DISCUSSION

As stated in the Introduction, the o-Ps lifetime can be related to the Ps cavity size where the annihilation takes place. Here we assume that the cavity can be approximated by a spherical potential well with radius R. The potential has an infinitely high wall and there is an electron layer with thickness ΔR on the wall surface. An additional assumption is that the Ps lifetime in a sample with no free volume is 0.5 ns. The relationship between the lifetime and the cavity radius R using these assumptions was derived by Nakanishi *et al.* as

$$\tau_3^{-1}=(2\,\mathrm{ns}^{-1})\{1-(R/R_0)+0.159[\sin(2\pi R/R_0)]\} \quad (1)$$

where $R_0 = R + \Delta R = R + 0.166\,\mathrm{nm}$[10]. The cavity volume (V_c) is calculated by the relationship

$$V_c = (4\pi/3)R^3 \qquad (2)$$

Figure 4 shows the plot of the 'Bondi' free volume of various liquids and polymers *versus* the cavity volumes, determined from our previous lifetime data[5,11] by using equations (1) and (2). In spite of the empirical nature of the approach, a clear correlation is found between the two parameters (correlation coefficient = 0.965). The correlation is well approximated by a straight line and is more suitable for quantitative analysis than the previous 'curved' correlation between the lifetime and the free volume. The relationship obtained by a least squares analysis is $V_f(\mathrm{cm^3\,g^{-1}}) = 1.51\,V_c(\mathrm{nm^3})$.

According to the free volume theory of diffusion, the gas diffusion coefficient is related to the free volume by the following:

$$D = A\exp(-B/V_f) \qquad (3)$$

where A and B are constants which depend on the gas being considered. The diffusion coefficients of Ar, N_2 and O_2 in various polymers were determined by Haraya and Hwang[12]. These authors deduced the numerical values of A and B by fitting the measured D-values to equation (3).

Figure 5 depicts plots of the diffusion coefficients of Ar, O_2 and N_2 in various polymers (as reported by Haraya and Hwang[12]) *versus* the inverse of the *o*-Ps cavity volumes, with the latter determined from our previous lifetime data[5,11]. As expected from the free volume model of equation (3) and the correlation seen in *Figure 4*, the logarithm of the diffusion coefficient decreases linearly with inverse cavity volume in all of the cases.

Quantitative values for the free volumes in the PEEK samples can be evaluated by first converting the lifetime data presented in *Figure 1* to the cavity volume through equations (1) and (2), and then to the free volume through the empirical relationship found from *Figure 4*. Free volume contents determined in this way are given in *Tables 1* and *2*. Also included in *Table 1* are the free volume contents of the amorphous film samples determined from the diffusivity data presented in *Figure 3*, by using equation (3) with the A- and B-values given by Haraya and Hwang[12]. Both sets of data in *Table 1* show that the effect of irradiation on the amount of the free volume of PEEK is small; the free volume is decreased by only a few percent (i.e. relative %) when the samples are irradiated with the maximum dose of 50 MGy. The effect of the irradiation on the amount of the free volume in the amorphous region of the

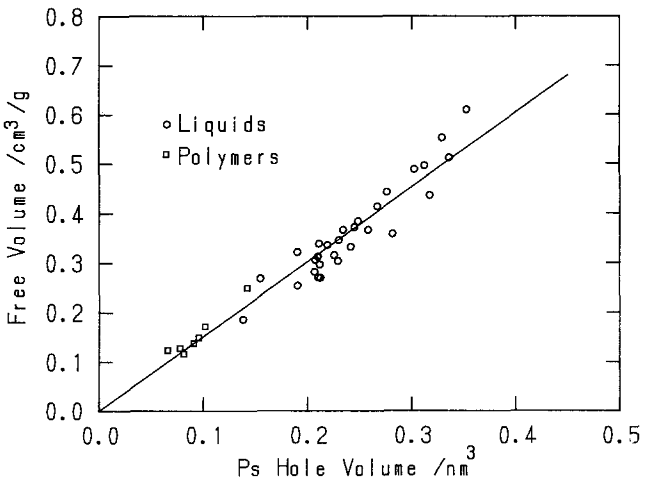

Figure 4 Plot of 'Bondi' free volume *versus* *o*-Ps cavity volume for various liquids (hydrocarbons, alcohols, ethers and pyridine) and polymers[5] at room temperature. The solid line represents the relationship V_f (cm^3 g^{-1}) = 1.51V_c(nm^3); the maximum deviation from this relationship is 16%

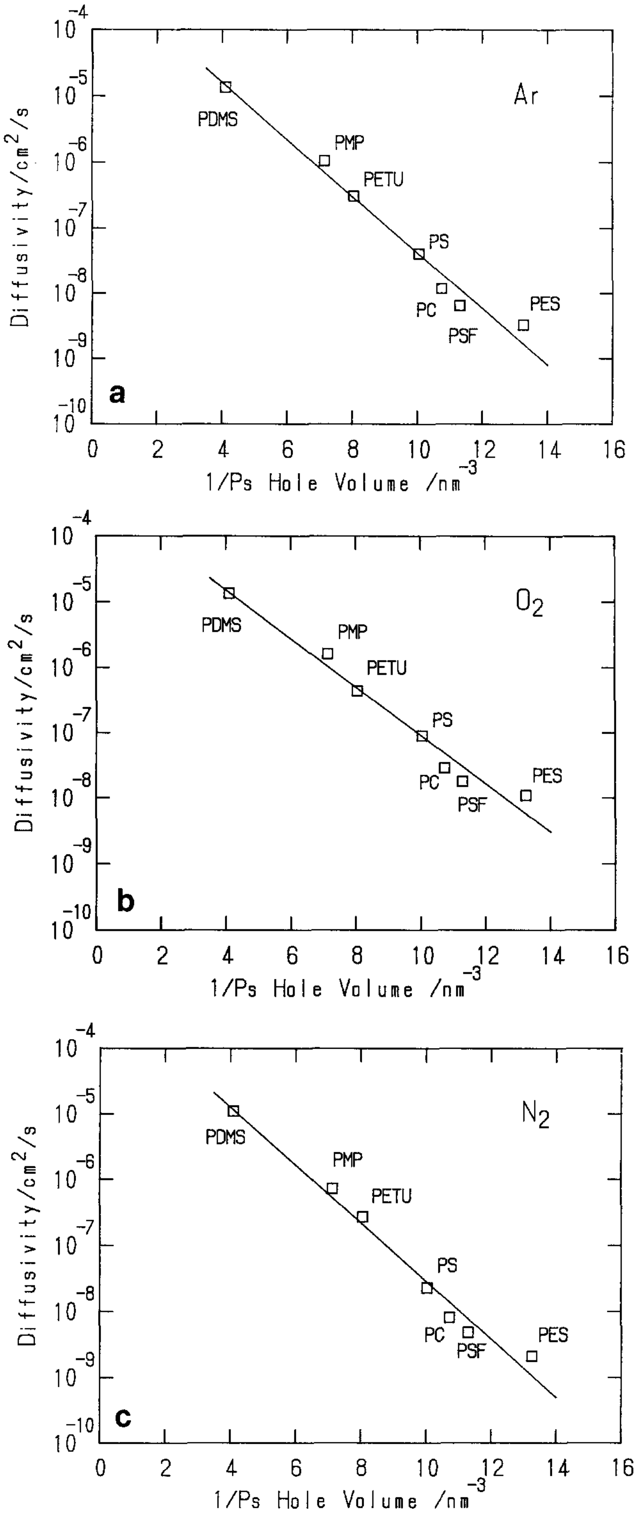

Figure 5 Plots of the diffusivities of Ar (a), O_2 (b) and N_2 (c) in various polymers *versus* the inverse of the *o*-Ps cavity volume: PDMS, poly(dimethylsiloxane); PMP, poly(4-methyl-1-pentene); PETU, poly(ether urethane); PS, polystyrene; PC, polycarbonate; PSF, polysulfone and; PES, poly(ether sulfone)

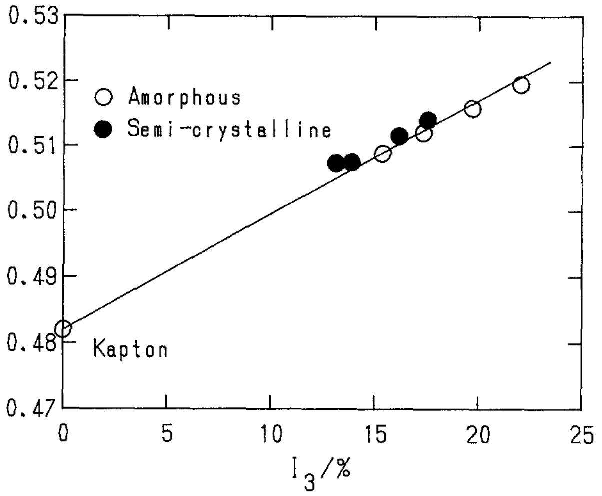

Figure 6 Plot of S *versus* I_3 for irradiated PEEK samples. Data for Kapton, where no Ps is formed, are also included

Table 1 Free volumes of electron irradiated amorphous PEEK samples determined from *o*-Ps lifetimes and diffusion coefficients of Ar, O_2 and N_2

Dose	V_f (cm^3 g^{-1})				
(MGy)	Bondi[a]	*o*-Ps	Ar	O_2	N_2
0	0.123	0.110	0.122	0.125	0.125
10	–	0.109	0.121	0.126	0.124
30	–	0.107	0.119	0.121	0.121
50	–	0.108	0.118	0.121	0.120

[a] Free volumes of the irradiated samples cannot be determined by the Bondi method[6] because of unknown molecular structures

Table 2 Free volumes of electron irradiated semicrystalline PEEK samples determined from *o*-Ps lifetimes

Dose (MGy)	V_f (cm^3 g^{-1})[a]
0	0.111
10	0.108
30	0.109
50	0.106

[a] V_f = total free volume contained in the amorphous region (1 g) of the semicrystalline sample

semicrystalline sample may be similar, as can be seen from *Table 2*. Decrease in the free volume may be related to intermolecular cross-linking, because the soluble fraction of the sample in 1-chloronaphthalene at 240°C becomes less and less as the dose increases[13]. Taking into account the errors involved in these measurements, agreement between the values of the free volume obtained by the two methods is fairly good.

The *o*-Ps intensity is sometimes considered to be proportional to the number of pre-existing free volume holes[14]. However, the fact that the free volume of the amorphous PEEK samples estimated solely from the *o*-Ps lifetime (and not from both the intensity and the lifetime) agrees with that determined from the gas diffusivity measurements suggests that the intensity change of about 30% (relative%) shown in *Figure 1b* does not indicate any effect of the irradiation on the free volume. In order to compare the irradiation effect on *p*-Ps with that on *o*-Ps we plotted the S-parameters of *Figure 2 versus* the I_3 values of *Figure 1*. The linear correlation which is obtained (see *Figure 6*) shows that the irradiation reduces the number of *o*-Ps and *p*-Ps atoms in such a manner that the *ortho–para* ratio is kept constant. Some active species formed by the irradiation may scavenge Ps precursors such as electrons, positrons and/or hot Ps atoms to inhibit the formation of both *o*-Ps and *p*-Ps atoms in the terminal positron spur[15].

CONCLUSIONS

A previously found correlation between the *o*-Ps lifetime and the free volume was improved by using the *o*-Ps cavity size as a new parameter. A quantitative relationship was found between the *o*-Ps cavity size and the total free volume of various molecular liquids and polymers. The free volume of electron irradiated PEEK samples was determined from the *o*-Ps lifetimes, based on the improved correlation and separately from the method using the diffusion coefficients of Ar, N_2 and O_2. Consistent results were obtained by the two methods and it was found that the effect of irradiation on the free volume of PEEK was rather small.

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