

## Hole size distributions in cardo-based polymer membranes deduced from the lifetimes of ortho-positronium

Y Kobayashi<sup>1,3</sup>, A Kinomura<sup>1,6</sup>, S Kazama<sup>2</sup>, K Inoue<sup>3</sup>, T Toyama<sup>3</sup>, Y Nagai<sup>3</sup>, K Haraya<sup>4</sup>, H F M Mohamed<sup>5</sup>, B E O'Rourke<sup>1</sup>, N Oshima<sup>1</sup>, R Suzuki<sup>1,7</sup>

<sup>1</sup>Research Institute for Measurement and Analytical Instrumentation, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan

<sup>2</sup>Nippon Steel & Sumitomo Metal Corporation, Technical Development & Planning Division, 6-1 Marunouchi, 2 chome, Chiyoda-ku, Tokyo 100-8701, Japan

<sup>3</sup>The Oarai Center, Tohoku University, Oarai, Ibaraki 311-1313, Japan

<sup>4</sup>Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

<sup>5</sup>Physics Department, Faculty of Science, Minia University, P. O. Box 61519, Minia, Egypt

E-mail: r-suzuki@aist.go.jp

**Abstract.** To clarify the free volume size distributions of the cardo-based polymer membranes, where ortho-positronium (o-Ps) undergoes pick-off annihilation, the o-Ps lifetime distributions were analyzed by the LT9 programme. It was found that the cardo-based polysulfone membrane has much narrower o-Ps lifetime/hole size distributions than the cardo-based polyimide membranes with the 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) moiety. Further, the lifetime/hole size distributions of the cardo-based polymer membranes are appreciably broadened with increasing temperature. This suggests that in these membranes there are holes not only of different sizes but also of different thermal expansion coefficients. It is also shown that in a membrane with a wider hole size distribution the average o-Ps lifetime tends to be longer than would be expected from the correlation between the o-Ps lifetime and the total free volume for common polymers.

### 1. Introduction

Introduction of a bulky cardo moiety into a polymer main chain is expected to hinder the molecular packing. The free volume model of gas diffusion states that the diffusivity of gas molecules in polymers depends on intermolecular open space often called free volume [1,2]. According to this model, sparse molecular packing with large free volume is advantageous to higher gas diffusivity. Therefore cardo-based polymers arouse interest for their application in gas separation membranes [3].

Positron annihilation lifetime spectroscopy (PALS) has been extensively used to study the nanostructure of amorphous polymers [4,5]. Some of the positrons injected into a polymer in many cases form the bound state with an electron, positronium (Ps). The experimental positron lifetime

<sup>6</sup>Present address: Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan

<sup>7</sup>To whom any correspondence should be addressed.



spectrum is usually resolved into three exponentially decaying components with lifetimes  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$  ( $\tau_1 < \tau_2 < \tau_3$ ) and the corresponding relative intensities  $I_1$ ,  $I_2$ ,  $I_3$ . The three lifetimes are attributed to the self-annihilation of spin parallel para-positronium (p-Ps), annihilation of non-Ps positrons with surrounding electrons, and pick-off annihilation of o-Ps, in which the positron in o-Ps undergoes annihilation with one of the surrounding spin antiparallel electrons. According to Tao [6], Eldrup and others [7], the pick-off annihilation lifetime of o-Ps can be related to the size of a hole for o-Ps localization. Under a simplified assumption that the holes in a polymer are of spherical shape, the relationship between the pick-off annihilation lifetime ( $\tau_3$ ) of o-Ps and the average radius ( $R$ ) of the holes is given by

$$\tau_3 = 0.5 \left\{ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right\}^{-1} \quad (1)$$

where  $R_0 (= R + \Delta R)$  is the radius of an infinitely deep square well potential and  $\Delta R (= 0.166 \text{ nm})$  is the measure of the overlap of the Ps wave function with electrons on the walls of the open spaces. The hole volume  $V_h$  in  $\text{nm}^3$  is obtained as

$$V_h = \frac{4\pi}{3} R^3$$

This model, in spite of its simplicity, has been successfully applied to the study of a variety of functional polymers [8].

Recently we applied PALS to a series of cardo-based polyimide and polysulfone membranes [9]. It was found that acid anhydride moiety of polyimide membranes has a strong impact on Ps formation in the sense that no Ps forms in most of the polyimides with pyromellitic dianhydride and 3,3',4,4'-biphenyltetracarboxylic dianhydride moieties with high electron affinity, whereas favourable amounts of Ps are formed in those with 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) moiety with lower electron affinity. Favourable Ps formation was also observed for the cardo-based polysulfone membrane. It has been reported that Ps formation in polysulfones is little influenced by the presence of chemical groups or additives with high electron affinity due to the so-called anti-inhibition effect of  $-\text{SO}_2-$  groups on Ps formation [10,11]. Furthermore we studied the connectivity between the average hole size of cardo-based polymer membranes deduced by the Tao-Eldrup model and the gas diffusion coefficients. Logarithmic plots of the diffusion coefficients of  $\text{O}_2$  and  $\text{N}_2$  versus reciprocal average hole size for cardo-based polymers, based on the free volume theory of diffusion, are appreciably shifted from the previously reported correlations for common polymers. The shifts likely originate from the strong tendency of o-Ps staying in larger holes, which is possibly associated with wide hole size distributions of the cardo-based polymer membranes. This paper focuses on the o-Ps lifetime/hole size distributions of the three cardo-based polymer membranes with favourable Ps formation.

## 2. Experimental

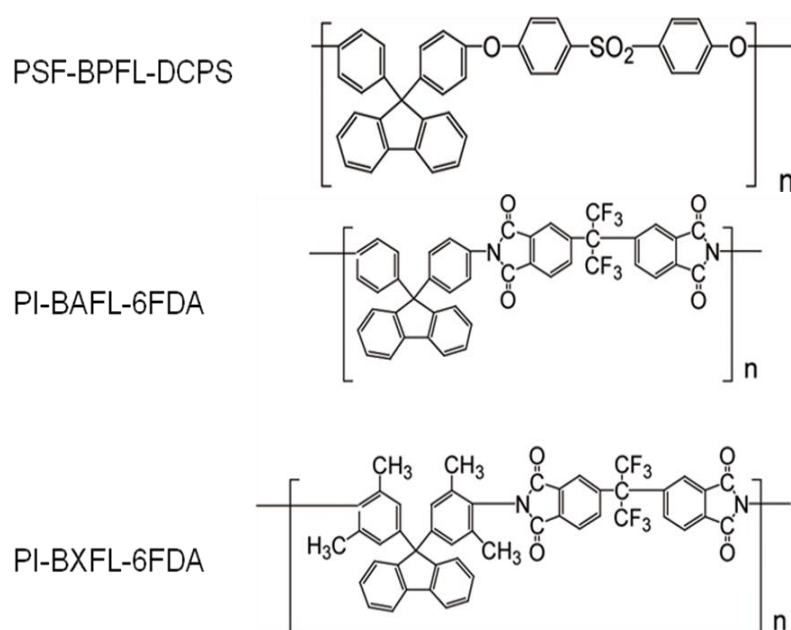
Figure 1 shows the chemical structures of cardo-based polymers studied [9]. The polymers have bis(phenol)fluorene, bis(aniline)fluorene or bis(xylidine)fluorene as the cardo moiety. Cardo polysulfone was supplied by Nippon Steel Corporation. Cardo-polyimides were synthesized by solution polycondensation reactions [3]. The abbreviations of the polymers follow the notation of X-Y-Z, where X means the type of the polymer; X = PI for polyimide and X = PSF for polysulfone. Y and Z are the abbreviations of bifunctional monomers: Y = BXFL for bis(xylidine)fluorene, Y = BAFL for bis(aniline)fluorene, Y = BPFL for bis(phenol)fluorene, Z = 6FDA for 2,2-bis(3,4-dicarboxyphenyl)

hexafluoropropane dianhydride, Z = DCPS for 4,4'-dichlorodiphenyl sulfone. The total free volume  $V_f$  of polymer was calculated from the following

$$V_f = V - V_0$$

where  $V$  is the specific volume and  $V_0$  the occupied volume. The occupied volume was estimated from the van der Waals volume ( $V_w$ ) according to the relationship  $V_0 = 1.3V_w$  [12].

Positron lifetime measurements were performed in a temperature range from 323 K down to 10 K with a fast-fast analogue spectrometer as previously described [9]. The lifetime spectra were analyzed into three components with the LT9 programme [13], assuming log normal distribution of the o-Ps annihilation rates (reciprocal lifetimes). The analysis provided the average o-Ps lifetime ( $\tau_{av}$ ), dispersion of o-Ps lifetime distributions and the relative intensity as well as two shorter discrete lifetimes and their relative intensities. From the obtained dispersions, o-Ps lifetime distributions at different temperatures were computed. At least 3 million counts were collected for each lifetime spectrum, which enabled the reliable analysis of the o-Ps lifetime distribution. Further, by applying the Tao-Eldrup model, hole volume distributions were obtained.



**Figure 1.** Chemical structures of PSF-BPFL-DCPS, PI-BAFL-6FDA and PI-BXFL-6FDA [9].

### 3. Results and discussion

In LT9 log normal distribution is assumed for o-Ps annihilation rates  $\lambda$  ( $=1/\tau_3$ ).

$$\alpha_3(\lambda) = -(2\pi)^{-\frac{1}{2}} \sigma_3^{-1} \exp\left[-\frac{\{\ln(\lambda) - \ln(\lambda_{30})\}^2}{2\sigma_3^2}\right] \lambda^{-1} d\lambda$$

where  $\sigma_3$  is the dispersion of the distribution and  $\lambda_{30}$  is the peak annihilation rate of o-Ps. From this, the o-Ps lifetime distribution is given by

$$\alpha_3(\tau_3) = -(2\pi)^{-\frac{1}{2}} \sigma_3^{-1} \exp\left[-\frac{\{(\ln(\lambda) - \ln(\lambda_{30}))\}^2}{2\sigma_3^2}\right] \lambda^{-1} d\lambda \frac{d\tau_3}{d\lambda}$$

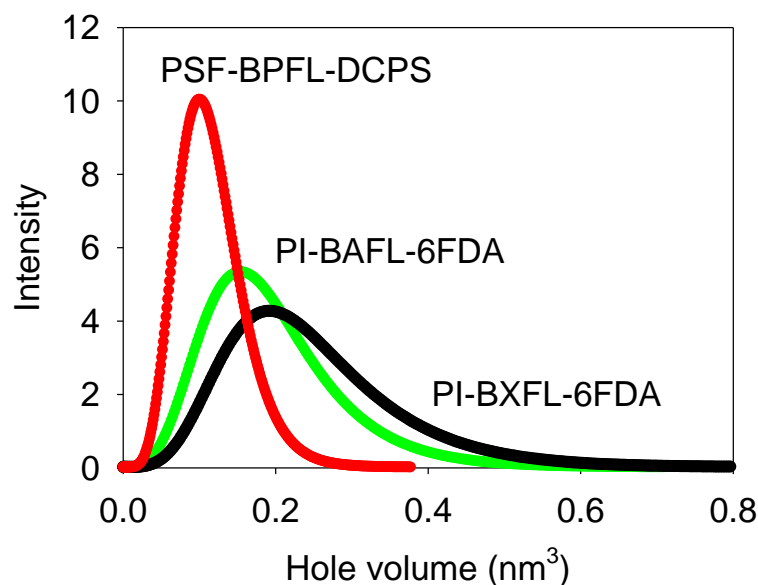
$$= (2\pi)^{-\frac{1}{2}} \sigma_3^{-1} \exp\left[-\frac{\{(\ln(\lambda) - \ln(\lambda_{30}))\}^2}{2\sigma_3^2}\right] \lambda d\tau_3$$

Further the hole volume distribution is expressed as

$$\alpha_3(V) = (2\pi)^{-\frac{1}{2}} \sigma_3^{-1} \exp\left[-\frac{\{(\ln(\lambda) - \ln(\lambda_{30}))\}^2}{2\sigma_3^2}\right] \lambda^{-1} d\lambda \frac{dV}{d\lambda}$$

where from equation (1),

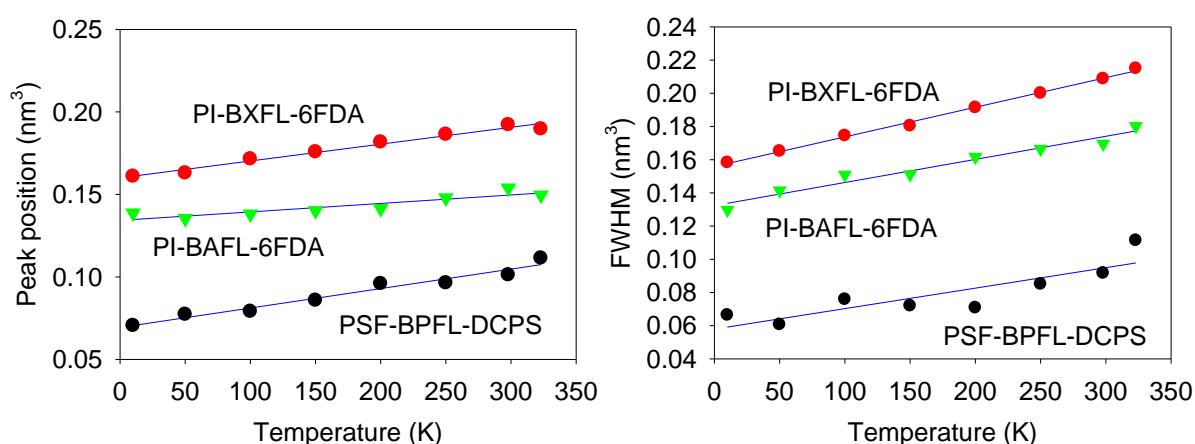
$$\frac{dV}{d\lambda} = -\frac{4\pi R^2 (R + R_0)^2}{2R_0} \left(1 - \cos \frac{2\pi R}{R + R_0}\right)^{-1}$$



**Figure 2.** Hole volume distributions of the three cardo membranes at 298K deduced from o-Ps lifetime distributions.

Figure 2 shows the distributions of hole volumes for PI-BXFL-6FDA, PI-BAFL-6FDA and PSF-BPFL-DCPS at 298 K obtained by the above equations. One can see that the distribution is broader in the order of PI-BXFL-6FDA > PI-BAFL-6FDA >> PSF-BPFL-DCPS. In figure 3 is shown the temperature dependence of the peak positions and full widths at half maximum (FWHM's) of the hole volume distributions deduced from the o-Ps lifetimes for the three membranes. For all the membranes peak positions gradually shift to higher values with increasing temperature, which is reasonably attributed to the thermal expansion of the open spaces for Ps localization. Larger hole volumes in PI-BXFL-6FDA than PI-BAFL-6FDA at all the temperatures studied may be attributed to the presence of the more bulky methyl substituted BXFL moiety in the former membrane [9]. In figure 3 we also note

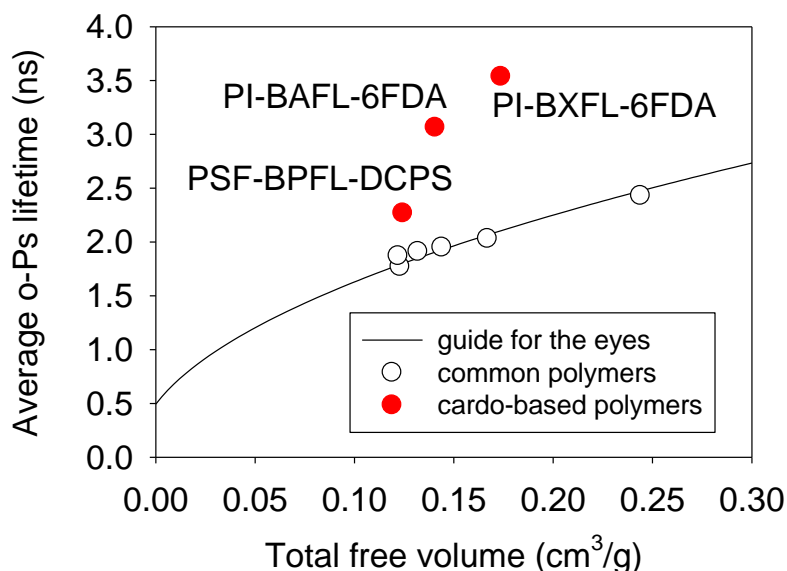
that at every temperature the distribution is broader (FWHM is larger) in the order of PI-BXFL-6FDA > PI-BAFL-6FDA >> PSF-BPFL-DCPS. It is conjectured that in the former two membranes because of the stiff chains of polyimide the structures around large intermolecular spaces are not able to relax sufficiently and molecular packing is hindered, resulting in the wide hole size distributions peaked at larger hole sizes. This is not surprising because Shimazu et al [14] reported that o-Ps lifetimes in other polyimides with 6FDA moieties are also widely distributed at room temperature. The lifetime/hole size distributions of the membranes, in particular, PI-BXFL-6FDA and PI-BAFL-6FDA are considerably broadened with increasing temperature, which suggests that in these cardo-based membranes there are holes of not only different sizes but also of different thermal expansion coefficients. In PSF-BPFL-DCPS, molecular chains are more flexible than polyimides [3, 9] and hence the distributions are much narrower and the holes are smaller.



**Figure 3.** Peak positions (left) and FWHM's (right) of the hole volume distributions of the three cardo-based membranes as a function of temperature.

Figure 4 shows the plot of the average o-Ps lifetime versus total free volume for common polymers such as polystyrene, polycarbonate and so forth [15] as well as the three cardo-based polymer membranes at 298 K. For common polymers, where the hole size distributions are not significantly broadened, there is a good correlation between the two quantities; the o-Ps lifetime systematically increases from 0.5 ns to higher values with increasing total free volume. However, the data points for PI-BXFL-6FDA, PI-BAFL-6FDA and PSF-BPFL-DCPS are all deviated upward from the correlation, indicating that the average o-Ps lifetimes in these polymers are appreciably longer than expected from the correlation for the common polymers. The deviation is the largest for PI-BXFL-6FDA and the smallest for PSF-BPFL-DCPS. Therefore, the broader the lifetime/hole size distribution in figure 2, the larger the deviation from the correlation for the common polymers in figure 4.

According to molecular dynamics simulation of polymers [14, 16], the holes in the amorphous region of polymers are not closed, with opening and well connected to each other. Therefore, in a polymer with a wide hole size distribution, Ps formed in a smaller hole may migrate quantum mechanically to a neighbouring larger hole through connecting channels. In a polymer with a particularly wide hole size distribution such as PI-BXFL-6FDA, such a process is repeated a number of times until o-Ps gets trapped in the largest available hole. Once trapped in the largest available hole, o-Ps cannot go back to the smaller hole because of reduced zero-point energy in it, which results in the average o-Ps lifetime considerably longer than that expected from the average size of the actual hole size distribution. This is likely the reason why the data points for PI-BXFL-6FDA, PI-BAFL-6FDA and PSF-BPFL-DCPS are deviated from the correlation for common polymers in figure 4.



**Figure 4.** Correlation between the average o-Ps lifetimes and the total free volume for common polymers such as polycarbonate, polystyrene, polysulfone, polyethersulfone etc at 298 K. The line shows the guide for the eyes under the assumption that the o-Ps lifetime in a polymer with no free volume is 0.5 ns. Included in the figure are the data for PI-BXFL-6FDA, PI-BAFL-6FDA and PSF-BPFL-DCPS at 298 K.

#### 4. Conclusion

Positron lifetime spectra for three cardo-based polymer membranes, PI-BXFL-6FDA, PI-BAFL-6FDA and PSF-BPFL-DCPS with favourable Ps formation, recorded at different temperatures, were analyzed by the LT9 programme and the o-Ps lifetime/hole size distributions were obtained. At each temperature, the hole size distributions are broader in the order of PI-BXFL-6FDA > PI-BAFL-6FDA >> PSF-BPFL-DCPS. The hole volume distributions of the membranes, in particular, PI-BXFL-6FDA and PI-BAFL-6FDA are considerably broadened with increasing temperature, which suggests that in these cardo-based membranes there are holes not only of different sizes but also of different thermal expansion coefficients. The average o-Ps lifetimes of the three cardo-based membranes at 298 K are considerably longer than expected from the correlation between the o-Ps lifetime and total free volume for common polymers. Quantum mechanical migration of o-Ps from smaller holes to larger holes in a polymer with a wide hole size distribution may be responsible for the appreciable upward deviations of the o-Ps lifetimes from the correlation for common polymers.

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