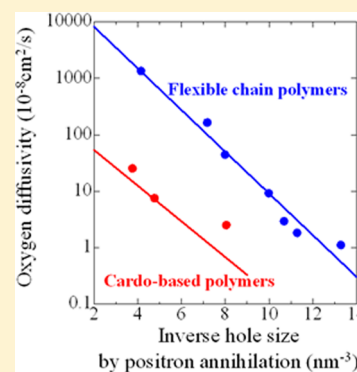


Positron Annihilation in Cardo-Based Polymer Membranes

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ABSTRACT: Positron annihilation lifetime spectroscopy (PALS) is applied to a series of bis(aniline)fluorene and bis(xylydine)fluorene-based cardo polyimide and bis(phenol)-fluorene-based polysulfone membranes. It was found that favorable amounts of positronium (Ps, the positron-electron bound state) form in cardo polyimides with the 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) moiety and bis(phenol)fluorene-based cardo polysulfone, but no Ps forms in most of the polyimides with pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA) moieties. A bis(xylydine)fluorene-based polyimide membrane containing PMDA and BTDA moieties exhibits a little Ps formation but the *ortho*-positronium (*o*-Ps, the triplet state of Ps) lifetime of this membrane anomalously shortens with increasing temperature, which we attribute to chemical reaction of *o*-Ps. Correlation between the hole size (V_h) deduced from the *o*-Ps lifetime and diffusion coefficients of O₂ and N₂ for polyimides with the 6FDA moiety and cardo polysulfone showing favorable Ps formation is discussed based on free volume theory of gas diffusion. It is suggested that *o*-Ps has a strong tendency to probe larger holes in rigid chain polymers with wide hole size distributions such as those containing cardo moieties, resulting in deviations from the previously reported correlations for common polymers such as polystyrene, polycarbonate, polysulfone, and so forth.



1. INTRODUCTION

Introduction of a bulky cardo moiety such as the bis(phenyl)-fluorene moiety into a polymer main chain provides better thermal stability, higher solubility, transparency, and so on. The four phenyl rings connected to a quaternary carbon in the bis(phenyl)fluorene moiety, for example, are expected to hinder the rotation of the phenyl groups and the molecular packing. According to the free volume model of gas diffusion, the diffusivity of gas molecules in polymers depends on the intermolecular open space, often called free volume. Therefore, the cardo-based polymers arouse interest in their application to gas separation membranes. Kazama et al. studied the CO₂ and N₂ transport properties of a series of bis(phenyl)fluorene-based cardo polymer membranes in comparison with non-cardo polymers containing bis(phenyl)isoprene moiety.¹

Positron annihilation lifetime spectroscopy (PALS) has been extensively used to study the nanostructure of amorphous polymers.^{2,3} A fraction of energetic positrons implanted into a polymer in many cases form the bound state with an electron, positronium (Ps). Singlet *para*-positronium (*p*-Ps) with the spins of the positron and electron antiparallel and triplet *ortho*-positronium (*o*-Ps) with parallel spins are formed at a ratio of 1 to 3. The self-annihilation of thermalized *p*-Ps results in the

emission of two photons with lifetime ~ 125 ps, whereas non-Ps positrons undergo two-photon annihilation after thermalization with one of the surrounding spin opposite electrons with lifetime 400–500 ps. The positron in *o*-Ps also undergoes two-photon annihilation with one of the surrounding electrons via a process known as pick-off annihilation. The lifetime of this process in *nonporous* polymers ranges from 1 to 5 ns and is strongly dependent on the size of sub-nanometer scale holes, where Ps is localized. The self-annihilation lifetime of *o*-Ps is about 142 ns, being much longer than the pick-off annihilation lifetime.

The experimental positron lifetime spectrum is usually fitted to a sum of three exponential components with lifetimes τ_1 , τ_2 , τ_3 ($\tau_1 < \tau_2 < \tau_3$) and the corresponding relative intensities I_1 , I_2 , I_3 . The three lifetimes are ascribed to the annihilation of *p*-Ps, non-Ps positrons, and *o*-Ps, whereas the intensities characterize the relative contributions from the three respective states to the overall positron lifetime spectrum. The following empirical relationship called the Tao-Eldrup model based on simplified

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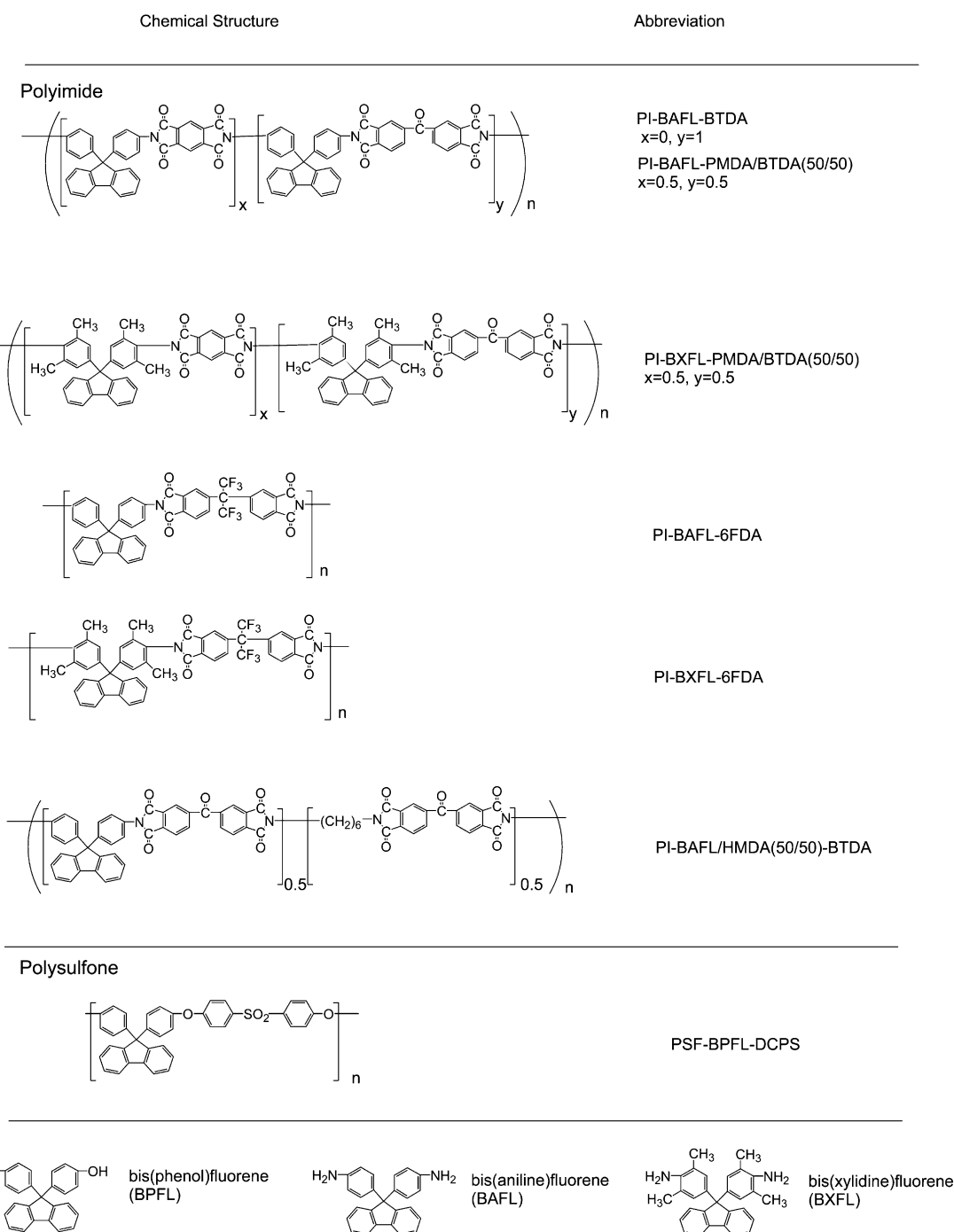


Figure 1. Chemical structures, name abbreviations of cardo polymers, and diamines used for synthesis.

assumptions allows the *o*-Ps pick-off annihilation lifetime $\tau_{\text{pick-off}}$ deduced by the three component analysis to be converted to the average radius (R) of spherical holes for Ps localization.

$$\tau_{\text{pick-off}} = 0.5 \left\{ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right\}^{-1} \text{ (ns)} \quad (1)$$

where $R_0 = R + \Delta R$ and ΔR ($=0.166$ nm for polymers) is the thickness of the homogeneous electron layer in which the positron in *o*-Ps is postulated to annihilate.^{4,5} The hole size V_h in nm^3 is obtained as

$$V_h = \frac{4\pi}{3} R^3 \quad (2)$$

The Tao-Eldrup model has been applied to the study of free volume in a variety of functional polymers⁶ such as gas separation membranes,^{7–11} polymer electrolyte membranes,^{12–14} reverse osmosis membranes,^{15–17} gas barrier films,^{18,19} and so forth.

In this study, we apply positron annihilation lifetime spectroscopy to bis(aniline)fluorene and bis(xylidine)fluorene-based cardo polyimide and bis(phenol)fluorene-based polysulfone membranes. First, the formation and annihilation of Ps in these membranes with different chemical structures are

investigated. Second, the relation between the hole size probed by Ps and gas diffusivities in the polymer membranes with favorable Ps formation is discussed.

2. EXPERIMENTAL SECTION

Figure 1 shows the chemical structures and name abbreviations of cardo polymers. The polymers have bis(phenol)fluorene, bis(aniline)fluorene, or multimethyl substituted bis(xylylene)-fluorene as the cardo moiety. Cardo polysulfone was supplied by Nippon Steel Corporation. Polyimides were synthesized via solution polycondensation reactions.¹ The abbreviations of the cardo polymers follow the notation of X-Y1/Y2(y1/y2)-Z1/Z2(z1/z2), 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 = BAFL for bis(aniline)fluorene, Y = BXFL for bis(xylylene)fluorene, Y = BPFL for bis(phenol)fluorene, Y = HMDA for hexamethylenediamine; Z = PMDA for pyromellitic dianhydride, Z = BTDA, for 3,3',4,4'-biphenyltetracarboxylic dianhydride, Z = 6FDA for 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride, Z = DCPS for 4,4'-dichlorodiphenyl sulfone. The mol % of Y and Z are given as y and z, respectively. The fractional free volume (FFV) of polymer was calculated from the following:

$$\text{FFV} = \frac{V - V_0}{V} \quad (3)$$

where V is the specific volume and V_0 the occupied volume of the polymer. The occupied volume was estimated from the van der Waals volume (V_w) according to the relation $V_0 = 1.3 V_w$.²⁰

Positron lifetime measurements were performed in a temperature range from 10 K to over 323 K with a fast–fast analogue spectrometer, whose time resolution is about 220 ps fwhm. An approximately 1 MBq sodium-22 source, sealed between two thin films of Kapton, was sandwiched between two stacks of polymer membranes with sufficient thicknesses to stop most of the positrons from the source. The sample-source-sandwich assembly was wrapped with an aluminum foil, set onto a copper plate and mounted on a coldfinger of a closed cycle helium refrigerator fitted to a vacuum tight chamber. Sample temperature was regulated with a heater attached to the copper plate and a precise temperature controller. Prior to the measurements all the samples had been conditioned under vacuum (~ 0.5 Pa) for longer than 24 h above 323 K for dehydration. Positron lifetime spectra were analyzed into three components using the PALSfit program,²¹ except those in which the long-lived *o*-Ps component is completely absent. The lifetime spectra with the long-lived *o*-Ps component were recorded at different temperatures upon cooling from the highest temperature down to 10 K. The measurements at 298 K after the completion of the cooling run ensured that there was no effect due to long-term positron irradiation of the samples, such as enhanced Ps formation caused by accumulation of trapped electrons.

Diffusion coefficients of O₂ and N₂ were measured by a high vacuum time lag apparatus (Rikaseiki Co.) at a constant temperature of 298 K. The apparatus is designed to keep up with a short time lag by connecting a fast response pressure transducer (MKS Baratron Model 317HS) directly to a gas permeation cell.¹ The gas diffusion coefficients (D) were calculated from the time lag measurement using the equation

$$D = \frac{l^2}{6L} \quad (4)$$

where l is the film thickness and L is the time lag.

3. RESULTS AND DISCUSSION

3.1. Formation and Annihilation of *o*-Ps in Cardo-Polymer Membranes. Table 1 lists the lifetime (τ_3) and

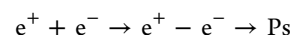
Table 1. Lifetime and Intensity of *o*-Ps at 298 K for the Cardo-Based Polymer Membranes Studied^a

membrane	<i>o</i> -Ps lifetime (ns)	<i>o</i> -Ps intensity (%)
PI-BXFL-6FDA	3.537 ± 0.006	27.30 ± 0.05
PI-BAFL-6FDA	3.064 ± 0.008	19.76 ± 0.06
PI-BXFL-PMDA/BTDA(50/50)	2.44 ± 0.06	1.02 ± 0.03
PI-BAFL-PMDA/BTDA(50/50)	-	no <i>o</i> -Ps
PSF-BPFL-DCPS	2.268 ± 0.006	22.38 ± 0.08
PI-BAFL/HMDA(50/50)-BTDA	-	no <i>o</i> -Ps
PI-BAFL-BTDA	-	no <i>o</i> -Ps

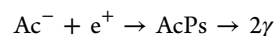
^aThe *o*-Ps component of PI-BXFL-PMDA/BTDA(50/50) with a relative intensity of only about 1% is clearly visible in the raw positron lifetime spectrum (8 million total counts and 150 background counts/channel).

intensity (I_3) of *o*-Ps at 298 K for the cardo-based polymer membranes studied. Large values of I_3 as much as 20% or higher are observed in PI-BXFL-6FDA, PI-BAFL-6FDA, and PSF-BPFL-DCPS, indicative of favorable Ps formation in these membranes. In PI-BXFL-PMDA/BTDA(50/50) I_3 is $\sim 1\%$ and a small amount of the positrons can form Ps. However, no Ps forms in PI-BAFL-PMDA/BTDA(50/50), PI-BAFL/HMDA(50/50)-BTDA, or PI-BAFL-BTDA.

According to the recombination (spur or blob) model of Ps formation,^{22–24} Ps is formed by a reaction between a positron and one of the electrons, liberated from the molecules by the energetic positron itself, in the end part (blob) of the positron track



where $e^+ - e^-$ stands for the correlated positron–electron pair (pre-Ps). In the presence of a strong electron acceptor, the liberated electrons, which otherwise can combine with the positron to form Ps, are deeply trapped by the electron acceptor (Ac). The resultant anion Ac^- captures the positron, which subsequently annihilates with a lifetime comparable to that of the non-Ps positron. As a result Ps formation is suppressed or totally inhibited.

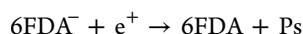


The chemical structure of the acid anhydride moiety in polyimide is known to have a significant impact on Ps formation.^{7,25} Of a large number of polyimides studied previously, I_3 of 6FDA-based polyimides is in the range from 7.1% to 19.1%. On the other hand, I_3 of PMDA and BTDA-based polyimides is at most 1%, and in many of them, no Ps forms at all. Electron affinities, EA, of the acid anhydrides are EA = 1.90 eV for PMDA, 1.55 eV for BTDA, and 1.39 eV for 6FDA.²⁵ Thus, EAs of the acid anhydrides are in the following order:



This conforms to the previous observation^{7,25} that many polyimides containing PMDA and BTDA moieties show no Ps formation, while those having 6FDA moieties exhibit Ps formation as much as $I_3 = 19.1\%$.

At least qualitatively, the discussion based on the recombination model can account for the different amounts of Ps formation in polymer membranes studied in the present work. PI-BAFL-PMDA/BTDA(50/50) contains PMDA and BTDA. PI-BAFL/HMDA(50/50)-BTDA and PI-BAFL-BTDA contain BTDA. In these polyimides, all the electrons in the end part of the positron track are tightly captured by PMDA and BTDA moieties with high EA and positrons are not able to combine with them at all, resulting in no Ps formation. The situation is similar to PI-BXFL-PMDA/BTDA(50/50) also containing PMDA and BTDA moieties except that a small number of electrons are somehow available for Ps formation in this membrane with the methyl substituted BXFL moiety. The large amounts of Ps formation in PI-BXFL-6FDA and PI-BAFL-6FDA are ascribed to the 6FDA moiety with lower EA. The electrons weakly captured by this moiety may be extracted by the thermalized positron to form Ps.



This means that the binding energy of Ps in 6FDA polyimides is larger than the electron affinity of 6FDA. The higher value of $I_3 = 27.3\%$ in PI-BXFL-6FDA in comparison with $I_3 = 19.8\%$ in PI-BAFL-6FDA suggests that electron donating methyl groups of the BXFL moiety of the former membrane somehow reduce the EA of 6FDA, making Ps formation more feasible. The $-\text{SO}_2-$ group in PSF-BPFL-DCPS is also an electron acceptor, but EA of this group is supposed to be lower than PMDA or BTDA. Previous studies^{14,26} revealed that the $-\text{SO}_2-$ group has the capability to recover Ps formation suppressed by other electron acceptors and acts as an anti-inhibitor of Ps formation. For a number of polysulfones I_3 is as much as 20% and this is also the case for PSF-BPFL-DCPS ($I_3 \approx 22\%$). The favorable Ps formation in PSF-BPFL-DCPS, as in other polysulfones, is due to the electron extraction by the positron from the $-\text{SO}_2^-$ -anion.^{14,26}

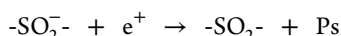
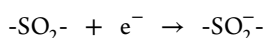


Figure 2 shows the temperature dependence of *o*-Ps lifetime and its relative intensity for PI-BXFL-6FDA, PI-BAFL-6FDA, PSF-BPFL-DCPS, and PI-BXFL-PMDA/BTDA(50/50) with Ps formation. The *o*-Ps lifetimes in the former three membranes with favorable Ps formation are monotonically elongated with increasing temperature; this is typical for a number of glassy polymers such as poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polyphenylene oxide (PPO),²⁷ in which *o*-Ps undergoes pick-off annihilation. The gradual elongation of the *o*-Ps lifetime with temperature is reasonably attributed to the reduced overlap of the Ps wave function with the surrounding electrons for the pick-off process as a result of the thermal expansion of the free space for Ps localization.

On the other hand the *o*-Ps lifetime in PI-BXFL-PMDA/BTDA(50/50) containing PMDA and BTDA moieties with high EA is progressively shortened with increasing temperature. Such *anomalous* shortening of the *o*-Ps lifetime with increasing temperature was previously observed for some polyimides in the glassy state.²⁸ It is likely that in PI-BXFL-PMDA/

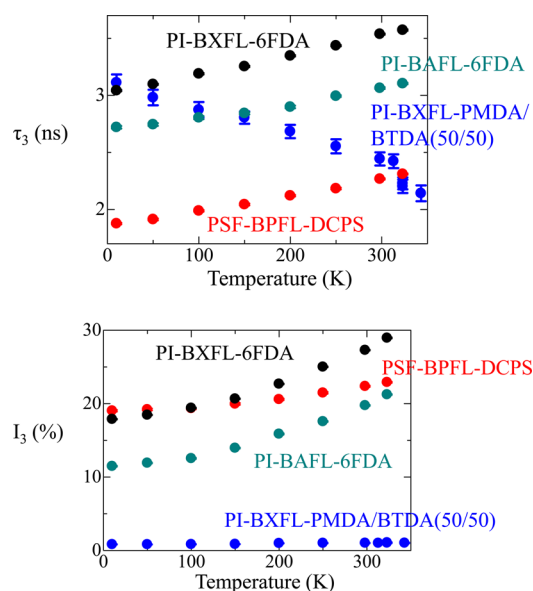
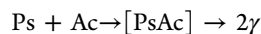


Figure 2. Temperature dependence of *o*-Ps lifetime (τ_3) and intensity (I_3) for PI-BXFL-6FDA, PI-BAFL-6FDA, PSF-BPFL-DCPS, and PI-BXFL-PMDA/BTDA(50/50) with Ps formation.

BTDA(50/50) Ps is quenched by chemical reaction with the electron accepting PMDA or BTDA moiety.



If Ps chemical reaction occurs, the annihilation rate of *o*-Ps (reciprocal *o*-Ps lifetime) is expressed as

$$\lambda_3 = \lambda_{\text{pick-off}} + kC \quad (5)$$

where $\lambda_{\text{pick-off}}$ is the *o*-Ps pick-off annihilation rate, k is the rate constant of the reaction, and C is the electron acceptor concentration.^{29–33} Quite a few studies conducted on chemical reactions of Ps with various electron acceptors in liquids and polymers revealed that in most cases the rate constant k increases with temperature.^{29,30,32} This implies the progressive shortening of the *o*-Ps lifetime at elevated temperatures, which is consistent with our observation for PI-BXFL-PMDA/BTDA(50/50) in Figure 2. The important consequence of this discussion is that we are not able to apply the Tao-Eldrup model to this membrane for the hole size estimation; substitution of measured τ_3 as $\tau_{\text{pick-off}}$ in eq 1 results in an incorrect hole size that is too small in comparison with that reflecting the molecular packing of PI-BXFL-PMDA/BTDA(50/50).

The data in Figure 2 also show that I_3 of PI-BXFL-6FDA, PI-BAFL-6FDA, and PSF-BPFL-DCPS increases with temperature but that of PI-BXFL-PMDA/BTDA(50/50) is essentially invariant. Unambiguous reasoning for these behaviors is not clear at present. Perhaps in the former three membranes the probability of electron extraction from the 6FDA[−] and $-\text{SO}_2^-$ -anions by the thermalized positron in the end part of the positron track is enhanced by heating due to thermal expansion, leading to increased Ps formation. Contrary to this, the thermalized positron may not play an important role in Ps formation in PI-BXFL-PMDA/BTDA(50/50) as is probably the case for chlorinated polyethylene with low I_3 .³⁴

3.2. Correlation between Gas Diffusion Coefficients and Hole Sizes Deduced from the *o*-Ps Pick-off Annihilation Lifetime for Cardo-Polymer Membranes

Table 2. Hole Radius (R) and Hole Volume (V_h) at 298 K Evaluated by the Tao-Eldrup Model for the Cardo Polymer Membranes with Favorable Ps Formation, Together with Their Glass Transition Temperature (T_g), Density, Fractional Free Volume (FFV), and Diffusion Coefficients (D_{O_2} and D_{N_2}) of Oxygen and Nitrogen

membrane	R (nm)	V_h (nm ³)	T_g (K)	density (g/cm ³)	FFV	D_{O_2} (cm ² /s)	D_{N_2} (cm ² /s)
PI-BXFL-6FDA	0.399	0.266	>673	1.22	0.212	2.50×10^{-7}	7.20×10^{-8}
PI-BAFL-6FDA	0.368	0.209	671	1.318	0.184	7.42×10^{-8}	1.60×10^{-8}
PSF-BPFL-DCPS	0.309	0.124	547	1.246	0.155	2.48×10^{-8}	4.30×10^{-9}

with Favorable Ps Formation. As is seen from the temperature dependence data in Figure 2, *o*-Ps undergoes pick-off annihilation, without being affected by Ps chemical reaction, in PI-BXFL-6FDA, PI-BAFL-6FDA, and PSF-BPFL-DCPS. Thus, it is possible to evaluate the hole size of these cardo-based membranes by applying the Tao-Eldrup model to the measured *o*-Ps lifetime τ_3 . Table 2 lists the hole radius (R) and hole volume (V_h) evaluated by the Tao-Eldrup model for the three membranes, along with their glass transition temperature (T_g), density, fractional free volume (FFV), and diffusion coefficients (D_{O_2} and D_{N_2}) of oxygen and nitrogen. V_h is 0.266 and 0.209 nm³ for PI-BXFL-6FDA and PI-BAFL-6FDA, respectively. The larger hole size of PI-BXFL-6FDA than PI-BAFL-6FDA appears to be rational because of the presence of more bulky methyl substituted BXFL moiety in the former membrane in between the stiff chains of polyimide that hinder the molecular packing. However, the hole volumes of PI-BXFL-6FDA and PI-BAFL-6FDA are smaller than some of other polyimides with the 6FDA moiety (e.g., 0.357 nm³ for TMPD)⁷ and it is not generally the case that the rotational hindering of the phenyl groups in the cardo-based polyimides leads to larger intermolecular space in comparison with other polyimides without the cardo moiety. The hole volume of PSF-BPFL-DCPS is 0.124 nm³ and much smaller than the polyimide membranes, which is likely due to the less stiff chains of this polysulfone ($T_g = 547$ K) than the polyimides ($T_g > 671$ K).

We performed decomposition of the positron lifetime spectra of PI-BXFL-6FDA at different temperatures into four components. It turned out that the four component analysis gave better fits to the raw spectra of PI-BXFL-6FDA but with much larger uncertainties of each component than the three component analysis. The four component analysis gave two *o*-Ps components: a shorter-lived *o*-Ps component with an almost temperature-invariant lifetime of about 1.9 ns and an intensity of ~8%, and a longer-lived *o*-Ps component with lifetime that increases from ~3.4 ns at 10 K to ~4.0 ns at 323 K and intensity increasing from ~13% at 10 K to ~23% at 323 K. In light of irregular, random molecular packing of amorphous polymers, it is difficult to contemplate two well-defined sites with definite sizes for *o*-Ps localization. Therefore, we rather consider that the splitting of the *o*-Ps lifetime into two different components with increased separations at elevated temperatures in the four component analysis reflects the wide size distribution of the hole sizes for *o*-Ps localization in polyimide⁷ and its broadening with temperature.

Studies of polymer structures by molecular dynamics simulation^{7,35,36} show that the holes in the amorphous structure of polymers are not closed, with openings that are irregular in shape and well connected to each other. Thus, the *o*-Ps atom formed in a smaller hole of a polymer has a chance to migrate quantum mechanically to a neighboring larger hole through connecting channels. In a polymer with a wider hole size distribution such a process is repeated a number of times and *o*-Ps spends a much longer time in larger holes because of its

much smaller zero-point energy inside them. The important consequence of this effect is that in a polymer with a wide hole size distribution such as cardo polyimides *o*-Ps has a strong tendency to stay in larger holes and its lifetime obtained by the three component analysis could be considerably longer than would be expected from the average size of the actual hole size distribution.

Based on free volume theory of diffusion in polymers,^{37,38} the gas diffusion coefficient is related to the fractional free volume (FFV) by the following:

$$D = A \exp(-B/FFV) \quad (6)$$

where A and B are constants which depend on the diffusant being considered. According to this equation the diffusion coefficient becomes higher in polymers with larger FFV. In the application of PALS to the study of polymer membranes a similar equation but with FFV replaced by the hole volume V_h determined by the Tao-Eldrup model is frequently used.

$$D = A' \exp(-B'/V_h) \quad (7)$$

The advantage of the latter approach is that PALS is applicable to polymers with unknown chemical structure or van der Waals volume³⁹ and also to thin films,^{40,41} for which FFV cannot be estimated. Figures 3 and 4 show the plots of diffusion

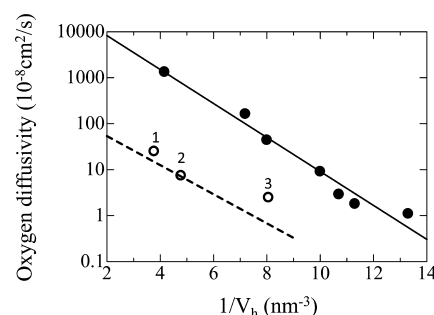


Figure 3. Logarithmic plot of oxygen diffusivity (D_{O_2}) versus inverse hole size (V_h) derived by the Tao-Eldrup model for PI-BXFL-6FDA (1), PI-BAFL-6FDA (2), and PSF-BPFL-DCPS (3). Also shown is the previously reported correlation⁴² for flexible chain polymers, poly(ether sulfone) (PES), polysulfone (PSF), polycarbonate (PC), polystyrene (PS), polyetherurethane (PETU), poly(methyl-1-pentane) (PMP), and polydimethylsiloxane (PDMS). The broken line displays the correlation for rigid chain polymers⁸ reported by Nagel et al.

coefficients of O_2 and N_2 , respectively, in PI-BXFL-6FDA, PI-BAFL-6FDA, and PSF-BPFL-DCPS versus inverse hole volume V_h . Also included in these figures are the plots for common polymers⁴² such as polystyrene, polycarbonate, and polysulfone. The good linear relationships for the common polymers indicate that not only is V_h a good measure of the free volume, but also A' and B' for O_2 or N_2 are constant for these polymers. The corresponding plots based on eq 6 are

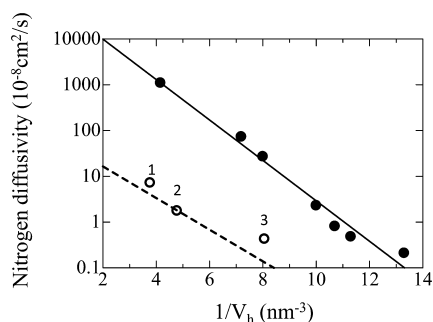


Figure 4. Logarithmic plot of nitrogen diffusivity (D_{N_2}) versus inverse hole size (V_h) derived by the Tao-Eldrup model for PI-BXDL-6FDA (1), PI-BAFL-6FDA (2), and PSF-BPFL-DCPS (3). Also shown is the correlation⁴² for the flexible chain polymers. The broken line displays the correlation for the rigid chain polymers⁸ reported by Nagel et al.

shown in Figures 5 and 6. We note that in Figures 3 and 4 the data for the 6FDA polyimides, PI-BXFL-6FDA, PI-BAFL-

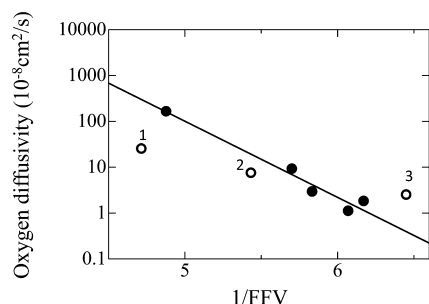


Figure 5. Logarithmic plot of oxygen diffusivity (D_{O_2}) versus fractional free volume (FFV) for PI-BXDL-6FDA (1), PI-BAFL-6FDA (2), and PSF-BPFL-DCPS (3). Also shown is the correlation for flexible chain polymers, PES, PSF, PC, PS, and PMP, for which FFV was estimated from the data⁴³ reported by Haraya and Hwang.

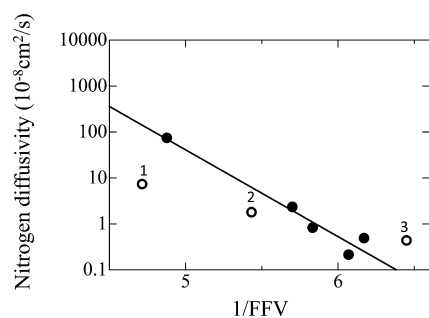


Figure 6. Logarithmic plot of nitrogen diffusivity (D_{N_2}) versus fractional free volume (FFV) for PI-BXDL-6FDA (1), PI-BAFL-6FDA (2), and PSF-BPFL-DCPS (3). Also shown is the correlation for the flexible chain polymers.

6FDA, are considerably shifted to the left from the correlations for the common polymers, but the shifts are not so large in Figures 5 and 6. The data points of PSF-BPFL-DCPS are also shifted to the left in Figures 3 and 4 but are situated closer to the correlations for common polymers in Figures 5 and 6.

Nagel et al.⁸ studied a series of rigid chain polymers, poly(amide imide), poly(ester imide), and polyimide, by PALS and found that the plots of the logarithm of the diffusion coefficients of O_2 and N_2 versus $1/V_h$ are deviated from the linear relationships for the common polymers. According to these authors A' in eq 7 is not a constant for different kinds of

polymers but depends strongly on the energy barrier for the diffusant gas molecule to overcome for a motional jump. Briefly, the larger energy barrier for stiff chain polymers with high T_g such as polyimide reduces A' and results in deviations of the correlations from flexible chain polymers with little barrier for the motional jump. In Figures 3 and 4 the points of PI-BXFL-6FDA and PI-BAFL-6FDA are almost on the same correlation for the rigid chain polymers by Nagel et al. However, the deviations of the points are not so distinctive if FFV is used as a measure of free volume instead of V_h in Figures 5 and 6. Here it should be mentioned that the lowering of A' is not only caused by the larger energy barrier for a motional jump of the diffusant, but also due to elongation of the o -Ps lifetime caused by preferred annihilation in the largest free volumes. In PI-BXFL-6FDA and also in PI-BAFL-6FDA the presence of bulky cardo-moieties and stiff chains of polyimide are supposed to considerably broaden the hole size distribution. As a result in these membranes o -Ps preferentially probes the larger holes and its lifetime tends to become longer than expected from the average hole size. This effect may play a certain role in the case of PSF-BPFL-DCPS as well, where because of the presence of the bulky cardo moiety the hole size distribution is likely wider than non-cardo polysulfone, which would elongate the o -Ps lifetime and result in deviations to the left from the correlations for the flexible chain polymers in Figures 3 and 4, but not in Figures 5 and 6.

The origin of the shifts of the points for cardo polymers from the correlations for common polymers in the plots based on free volume theory may be twofold: strong tendency of o -Ps staying in larger holes in polymers with wide hole size distributions such as those containing bulky cardo moieties, and stiff chains that increase the energy barrier for the diffusant gas molecule to overcome for a motional jump. Ps is a powerful probe to study the nanostructure and free volume of polymeric membranes, in particular, in cases where FFV cannot be estimated from the van der Waals volume, but one must be careful for the possible influence of hole size distribution on the o -Ps pick-off annihilation.

4. CONCLUSION

We have applied positron annihilation lifetime spectroscopy (PALS) to a series of cardo polyimide and polysulfone membranes. Favorable Ps formation was observed for polyimide membranes with the 6FDA moiety with lower electron affinity but no Ps forms in most polyimide membranes with PMDA and BTDA moieties with higher electron affinity. This conforms to the previous studies in the sense that the acid anhydride has an important impact on Ps formation in polyimide. Polyimide membranes containing the methyl-substituted BXFL moieties tend to show higher Ps yields than the non-methyl-substituted BAFL counterparts. As for the cardo-polysulfone membrane favorable Ps formation was observed. Variations of the o -Ps lifetimes with temperature revealed that o -Ps undergoes pick-off annihilation in the membranes with favorable Ps formation, without being influenced by chemical reaction of Ps. The hole volumes of PI-BXFL-6FDA and PI-BAFL-6FDA deduced by the Tao-Eldrup model are smaller than some of other polyimides with the 6FDA moiety, and it is not generally the case that the rotational hindering of the phenyl groups in the cardo-based polyimides leads to larger intermolecular space than other polyimides. Logarithmic plots of diffusion coefficients of O_2 and N_2 versus reciprocal hole size deduced by the Tao-Eldrup

model for the membranes with favorable Ps formation, based on the free volume theory of diffusion, are appreciably shifted from the previously reported correlations for common polymers with flexible chains. This may originate from the preferential staying of *o*-Ps in larger holes in polymers with wide hole size distributions. The shifts of the points for cardo polyimide membranes in the plots of diffusion coefficients of O₂ and N₂ versus 1/FFV suggest a role played by stiff chains of polyimide that increase the energy barrier for the diffusant gas molecule to overcome for a motional jump as previously suggested. The relationship between gas diffusivities and polymer free volume is not so simple and a number of factors have to be taken into consideration in the optimal design of gas separation membranes.

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Notes

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