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Free-Volume Distribution of High Permeability Membrane Materials Probed by Positron Annihilation

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ABSTRACT: Positron annihilation lifetime (PAL) spectroscopy was applied to measure free-volume size distribution in polymer samples with unusually long lifetimes: in dense films of poly(trimethylsilylpropyne) (PTMSP) and in porous membranes prepared from poly(phenylene oxide) (PPO). PAL data were treated by finite-term lifetime analysis (PATFIT program) and continuous lifetime analysis (CONTIN program). Lifetime distributions of positron annihilation in these samples consist of two positronium components: in the range 1−2 and 4−8 ns (PTMSP) and in the range 20−70 ns (porous PPO). In the case of PTMSP, the longer lifetimes correspond to continuous free-volume size distribution in the range $R = 4.5{-}5.5$ Å. These radii are much larger than those characteristic for "normal" glassy polymers. A good agreement was obtained between the parameters of PAL distributions obtained by means of PATFIT and CONTIN programs in PTMSP and PPO dense films. An analysis of the CONTIN peak widths of free-volume size distribution in different polymers both studied in this work and reported in the literature indicated that the ratio of peak width and average radius R_{av} levels off at larger sizes of free volume. An estimate of the diffusion coefficient of positronium was made for PPO samples with different surface area.

Introduction

Study of free volume (FV) in polymer systems is of great interest because the size and concentration of its elements (holes) affect numerous transport, mechanical, and other physicochemical properties of polymers. Positron annihilation lifetime (PAL) spectroscopy is now one of the most efficient approaches for investigations of FV (see, e.g., refs 1−5). The foundations of this method for probing polymers were based in particular on Walker−Brandt−Berko's free volume model.[6] According to this model, Positronium Ps (a bound atomic system which consists of an electron and the positron) tends to be localized or trapped before its annihilation in FV or, in other words, in areas with reduced electron density. Accordingly, annihilation characteristics (lifetimes and intensities of longer lifetime components of annihilation radiation) give information on concentrations, sizes, and distributions of FV.[7−9]

Until recently, most of the PAL data were analyzed in a finite-term lifetime approach. A computer program PATFIT, which represents annihilation lifetime distribution in a discrete manner, i.e., as a sum of several exponents, is employed for this purpose. Every exponent is characterized by its decay rate $\lambda_i = 1/\tau_i$ (in ns^{-1}) and intensity I_i (in %). Recently Gregory and Jean[10,11] proposed the use of continuous lifetime analysis. In this approach, the Laplace inversion program CONTIN originally developed by Provencher[12] for an analysis of fluorescence spectra is used to obtain the continuous probability density function of annihilation with a given lifetime from annihilation lifetime spectra. In this way one can obtain the size distribution of FV in polymers.

The CONTIN analysis of positron annihilation lifetime distribution of positrons was accomplished successfully in a number of polymers: epoxy polymers,[11] polystyrene,[13,14] and polycarbonates with different structures.[15] A common feature of most of these systems is that positron lifetime distribution in all cases consisted of three components (in finite-term analysis) or was well described by three peaks (in continuous analysis). The longer lifetime peak τ_3 is localized in vicinity of about 3 ns. This corresponds to the radii of FV in polymers about 2−4 Å.[7−9] However some polymers may contain much longer positron lifetimes, 6 ns or more, which correspond to a significantly larger FV. The first example of such a behavior is poly(trimethylsilylpropyne) (PTMSP) as finite-term (PATFIT) analysis has shown.[16] These results and the data of other techniques (methods of electrochromism[16] and spin probes,[17] wide-angle X-ray scattering,[17] density measurement) indicated that this material has an unusually large free volume. Examination of the structure−properties relationship of PTMSP and other polymers (polyacetylenes, polynorbornenes, etc.[18]) allows one to conclude that the combination of rigid polyene main chain and bulky trimethylsilyl group attached directly to the backbone chain is the main reason for this unusual behavior. Very long positron lifetimes in this material were confirmed as well by other authors.[19,20] However, recently comparable long positron lifetimes and large sizes of FV were reported for perfluorodioxole copolymers, amorphous materials having entirely different chemical structures.[21,22] Both types of polymers are characterized by unusually loose chain packing and low density (high free volume estimated via Bondi's method)

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Table 1. Comparison of Lifetime Distributions of Positron Annihilation in Dense Films of PTMSP and PPO Using PATFIT and CONTIN Programs

	PTMSP		PPO	
parameter	PATFIT	CONTIN	PATFIT	CONTIN
τ_1, ns	0.136 ± 0.006	0.13	0.141 ± 0.008	0.15
τ_2, ns	0.360 ± 0.010	0.40	0.370 ± 0.008	0.35
τ_3, ns	1.520 ± 0.012	1.75	1.780 ± 0.140	
τ_4, ns	5.580 ± 0.020	5.63	3.060 ± 0.130	2.30
I_1, %	23.90 ± 1.40	24.5 ± 0.4	18.35 ± 1.50	14.6 ± 1.2
I_2, %	29.40 ± 1.30	26.7 ± 0.7	50.46 ± 1.21	54.0 ± 2.0
I_3, %	5.58 ± 0.02	5.4 ± 0.8	15.38 ± 2.65	
I_4, %	40.50 ± 0.30	42.9 ± 3.0	15.80 ± 2.97	31.0 ± 0.6

and a very high level of the gas permeability, diffusion, and solubility coefficients as a consequence.

The purpose of this work is to compare the results of application of both programs: PATFIT and CONTIN for the treatment of positron annihilation characteristics obtained in studies of polymer samples distinguished by unusually long Ps lifetimes or, according to the existing conceptions, substantially larger sizes of FV. Dense films of PTMSP and both dense films and porous membranes prepared from poly(2,6-dimethylphenylene oxide) (PPO) were the objects of the investigation.

Experimental Section

PTMSP was synthesized by polymerization in the presence of catalytic system $TaCl_5$/triisobutylaluminum. The polymer had the intrinsic viscosity of 5.7 dL/g and M_w = 2 000 000 (GPC). The films were cast from the solution in toluene and dried in a vacuum oven at 40−50° C for several days until a constant weight was achieved. Dense films of PPO were cast from the solution in chloroform and prepared in the same manner. Porous PPO membranes obtained by the phase inversion method[23] with surface areas of 70 and 200 m^2/g were provided by Dr. F. P. Cuperus (ATO-Agrotechnology, The Netherlands) and used as received.

The measurements were performed using an ORTEC standard "fast−fast" coincidence circuit of positron lifetime spectrometer with time resolution 230 ps (full width at half-maximum (fwhm) of the prompt coincidence curve). Integral statistics for each PAL spectrum was at least 10^7 counts. A high purity and defect free single-crystal Silicon sample was used as a reference one. Its PAL spectrum consisted of a single component with lifetime 220 ps in agreement with the results of Dannefaer et al.[24] Measurements were carried out under atmospheric conditions, i.e., in contact with air.

Results and Discussion

Table 1 shows a comparison of PAL spectra in PTMSP and the dense PPO film obtained using PATFIT and CONTIN programs. It is seen that PPO reveals the spectrum typical for regular polymeric materials: the intermediate, positron lifetime component τ_2 is close to 0.4 ns, whereas the Ps component is in the range 2−3 ns. Although the PATFIT program allows one to recognize here two longer lifetime components τ_3 and τ_4, they do not distinguish between them markedly and they have a similar intensity, about 15%. The CONTIN program, which was used in the range of annihilation rates of 0.1−15 ns^{-1} (or lifetimes 0.06−10 ns) with 75 points in solution, describes them as one fairly broad peak with the maximum at 2.3 ns and intensity of 31%. The PATFIT treatment of annihilation data for PTMSP gave a lifetime τ_4 = 5.58 ns with a very large intensity of 40.5%. This is in a reasonable agreement with the results of a previous study[16] where another sample of PTMSP was investigated. A somewhat lower τ_4 value may be related to partial aging of this polymer.[17] The PATFIT and CONTIN data exhibit a very good agreement for PAL spectra of PTMSP, which can be considered as an evidence of an appropriate selection of the resolution function.

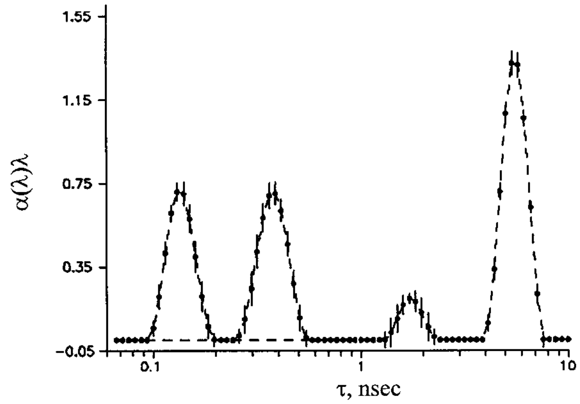

Figure 1. Lifetime distribution of PTMSP obtained by using the Laplace inversion program CONTIN.

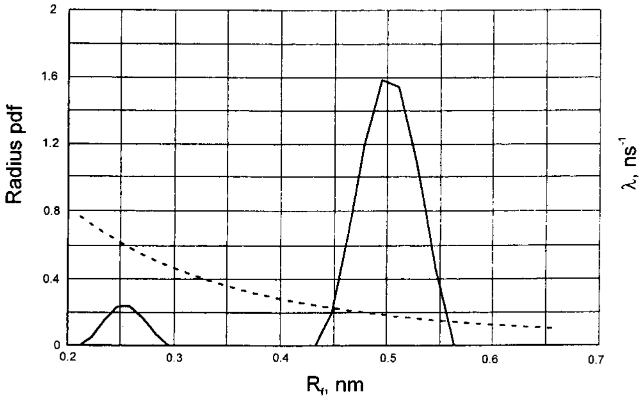

Figure 2. Free-volume hole radius distribution *R* pdf(*R*) of PTMSP obtained from the two right-hand peaks shown in Figure 1.

The probability density function $\lambda\alpha(\lambda)$ of annihilation with a rate λ for PTMSP at ambient temperature is shown in Figure 1. Using this distribution, size distribution of FV was calculated by means of an equation,[7,8] parameters of which were estimated in[25]

$$\tau_i = 0.5[1 - R_i/R_0 + (1/2\pi)\sin(2\pi R_i/R_0]^{-1} \quad (1)$$

where τ_i (i = 3 or 4) is expressed in nanoseconds, R_i and R_0 are in angstroms, and an empirical parameter $R_0 = R_i + \Delta R$, where ΔR = 1.656 Å. Naturally, size distribution consists of two peaks (Figure 2). The dashed line shows the calculated dependence of annihilation rate $\lambda_i = 1/\tau_i$ vs FV radius used in the computing of the size distribution by means of eq 1.

As it has been mentioned, the CONTIN method was extensively used for the determination of size distribution of FV in different polymers,[11,13,15,26,27] and this gives an opportunity for a comparison of FV in various materials. However, the CONTIN method needs a reference spectrum and high statistics. Recently, the performance of the CONTIN method and a novel method, the maximum entropy method (MELT), were compared.[28] It was shown that both CONTIN and MELT approaches provided excellent estimates of the intensities and the lifetimes of Ps components, although the latter required a smaller number of counts to

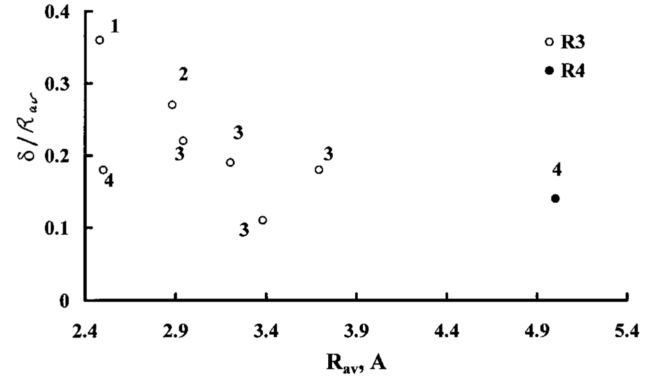

Figure 3. Dependence of dimensionless peak widths in size distributions of FVE on average (maximum) radius R_{av} in different polymers: 1, polyepoxide;[11] 2, polystyrene;[13] 3, different polycarbonates;[15] 4, PTMSP (this work). Open points correspond to the τ_3 components; the filled point corresponds to the τ_4 component of PTMSP.

Table 2. Width of Peaks δ in the CONTIN Size Distribution of FV in Polymers at Ambient Temperature

polymer	R, Å	δ (Å)	ref
polystyrene	2.88	0.77	13
polyepoxide	2.48	0.89	11
polycarbonate	2.94	0.64	15
tetramethyl polycarbonate	3.20	0.61	15
hexafluoro polycarbonate	3.38	0.37	15
hexafluorotetramethyl polycarbonate	3.69	0.68	15
PTMSP	2.5	0.46 (τ_3)	this work
	5.0	0.70 (τ_4)	

achieve the same standard deviation. Therefore we can compare the widths of Ps peaks in the cases of monomodal FV size distribution (polymers with "normal" free volume like polystyrene, polycarbonates, etc.) and bimodal size distribution (the polymer with unusually large free volume—PTMSP). For the latter material, the full width at half-maximum δ of the right-hand peak (Figure 2) corresponding to the fourth component τ_4 is equal to 0.7 Å. The corresponding δ value for the third component τ_3 is only 0.46 Å. The values of δ, which correspond to FV size distributions described by τ_3 and τ_4 components of various polymers, are given in Table 2. It can be concluded that the widths of the peaks of FV size distributions do not change substantially when the average size R_{av} of FV is increased from 2.5 to about 5 Å. If we take the dimensionless ratio δ/R_{av} as a relative measure of the width of size distribution, a monotonic decrease in this ratio is observed for different polymers with the average radius R_{av3} of FV (Figure 3). It should be noted that the ratio δ/R_{av} for R_3 in PTMSP is smaller than those of other glassy polymers, whereas the ratio for R_4 is larger, if one assumes linear extrapolation of the δ/R_{av} ratio in the range of radii from 2 to 3 to about 5 Å. It will be interesting to study size distribution of FV in other materials, which show extra-long lifetime components by PAL. This work is now in progress.

Let us consider now the results of the investigation of porous PPO membranes. Figure 4 gives the probability density function $\lambda\alpha(\lambda)$ of annihilation with a rate λ for the Ps part of the PAL spectra obtained by CONTIN analysis of the results for the samples with surface areas of 70 and 200 m^2/g. A total of 90 points were used for solution in the wider range of annihilation rates $\lambda = 0.01-15$ ns^{-1}. It should be noted that the weak peak at the lower curve, which is fully in the range of experimental error, was excluded from consideration, and we shall not interpret it below. The right-hand peak (Figure 4, curve 2) is shifted into a region of longer times τ_4; besides, its intensity is much larger. As can be seen, the long lifetime component of the Ps spectrum of the sample with surface area 200 m^2/g having an intensity (according to PATFIT analysis) equal to 6.5% is characterized by an average lifetime of 35 ns even under atmospheric conditions, i.e., in the presence of oxygen. This is somewhat higher than the τ_4 values previously reported using PATFIT analysis for the same material.[9] As has been noted in this work, the application of eq 1 at such long lifetimes is not completely accurate, because neglecting of the intrinsic annihilation rate of triplet Ps ($\lambda = 0.007$ ns^{-1}) in comparison with Ps annihilation in FV is not fully justified. A correction proposed by us[9] leads to somewhat larger pore radii (approximately by a factor of 1.3) if compared with eq 1. Therefore we must conclude that the PPO sample with a surface area of 200 m^2/g contains pores with a radius of about 14 Å.

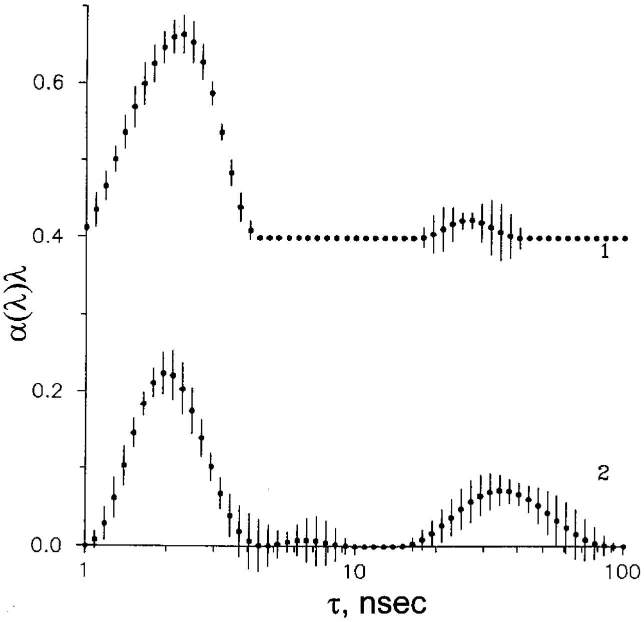

Figure 4. Positronium lifetime distribution of the two porous samples of PPO: 1, surface area is 70 m^2/g; 2, surface area is 200 m^2/g.

It would be interesting to find a relation between pore volume, pore size distribution, and surface area as determined by standard methods such as helium and mercury porometry or the BET method and the results of an application of the PAL method. Indeed, Venkateswaran et al.[30] found a positive correlation connecting surface area in porous materials and the intensity of a long-lived Ps component (I_4 in the designation of the present work). Interestingly, it does not involve the other parameter of PAL spectrum, i.e., the long-lived lifetime τ_4 . The polymeric materials studied in the present work encompass a wide range of surface areas: since that of PTMSP dense films has been reported[31] to be as large as 550 m^2/g, this property varied in the materials studied within nearly 1 order of magnitude. Hence, further exploration of this correlation is possible. Although, as seen from the data given below, an increase in surface area is accompanied by the growth of intensity I_4:

material	porous PPO membrane		PTMSP dense film
surface area, m^2/g	70	220	550
I_4, %	2	7.1	40.5

there is no quantitative agreement with the empirical correlation reported in ref 30 . It seems more likely that the surface area could be manifested in both I_4 and τ_4 parameters of the PAL spectra.

The study of these samples permits one as well to estimate the diffusion coefficients of Ps in the polymer matrix before its localization in a FV, which is important for the methodology of PAL spectroscopy for probing free volume structure in polymers. A strong variation of the intensity of the long-lived peak due to the variation of the surface area infers that Ps diffusion length l_{Ps} is comparable with an average distance between the pores in PPO membrane material. This statement is in agreement with the plausibly uniform morphology of porous membranes obtained by the phase inversion method.[23] The assumption made above leads[29] to the following inequality for l_{Ps}: $3 \times 10^{-7} < l_{Ps} < 5 \times 10^{-7}$cm. Bearing in mind that $l_{Ps} = (6D_{Ps}\tau)^{1/2}$, with τ representing the nonlocalized Ps lifetime, one can obtain the following estimate for the diffusion coefficient of nonlocalized Ps:

$$5 \times 10^{-5} < D_{Ps} < 1.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$$

The lower limit is rather close to the value reported in ref 30 for the cross-linked resins and equal to 1.5×10^{-5} cm^2 s^{-1} and is somewhat lower than D_{Ps} in the amorphous part of ice.[32] The D_{Ps} values found by us and in refs 30, 32 are significantly larger that the diffusion coefficient of localized Ps equal to 3×10^{-6} cm^2 s^{-1} which was found in quenching experiments in different glassy polymers (polycarbonate, polysulfone, polystyrene).[33] It favors the conception that it is Ps and not free positrons having much larger diffusion coefficients $D_+ = 0.1$ cm^2 s^{-1} (according to Maurino and Brandt[34]) which diffuse before annihilation. An alternative hypothesis, which should be, hence, discarded, is that positrons after diffusion are localized in a pore where they form Ps. It can also be noted that the accuracy of such estimation can be increased in studies with oxygen-free samples.

In conclusion, this work contains the first report of the lifetimes and FV (hole) size distributions in polymers distinguished by an unusually loose structure (high free volume): PTMSP and microporous PPO membranes. It was shown that PATFIT and CONTIN descriptions of annihilation data are in reasonable agreement: maxima of CONTIN peaks coincide with the τ_i component in PATFIT finite-term spectra. Bearing in mind some advantages noted for the MELT program (better accuracy of a description at lower statistics), it is planned to apply this approach as well for the analysis of FV size distribution in highly permeable polymers. On the other hand it will be useful in future to compare the results of application of different programs (CONTIN, MELT) for hole size distribution in samples with well-defined microstructures, for example zeolites.

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