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Temperature dependence of free volume distributions in polymers studied by positron lifetime spectroscopy

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Abstract

The temperature dependence of mean ortho-positronium lifetime ($\bar{\tau}_3$) and intensity (I_3) was measured in the range between 60 and 293 K for polycarbonate and polyoxymethylene samples. The values of $\bar{\tau}_3$ and I_3 are a constant below $T = 127$ K. Above this temperature the $\bar{\tau}_3$ as well as I_3 are a linear function of T . Annihilation lifetime measurements have also been performed to deduce the free-volume hole distributions in the polycarbonate and polyoxymethylene polymer samples at temperature of 70 and 293 K. Lifetime spectra were analysed using the Laplace transform and the hole volume distributions are determined from the results of o-Ps lifetime distributions using the particle in a spherical box theory. The free-volume hole radii of polycarbonate at 293 K are distributed between 2.1 and 3.9 Å with a maximum at (2.83 ± 0.02) Å. Free volumes spread out between 40 and 230 Å³ with a maximum at (92 ± 2) Å³. In the case of polyoxymethylene, the free volume hole radii at 293 K are peaked at (3.10 ± 0.07) Å inside (2.0 - 4.6) Å interval. Free volumes are distributed between 35 and 350 Å³ with a maximum at (125 ± 8) Å³. At ~75 K the distributions are quite different. They are narrower and shifted to lower values of R (V). In the case of polyoxymethylene, mean value of radius is (2.06 ± 0.02) Å and mean free volume is (35 ± 2) Å³. In the case of polycarbonate, mean radius is (2.5 ± 0.05) Å and the mean free volume is (70 ± 4) Å³.

Introduction

It becomes more clear that the concept of free volume [1] is very useful for understanding of macroscopic physical properties of the polymers. The size and concentration of free volume holes in polymers determine e.g. polymer chain dynamics, diffusion processes and rheological properties. The temperature dependence of the hole free volume, especially the change of it through the glass transition region and below T_g is very important to describe the physical ageing of polymers.

In spite of considerable effort in the theoretical development of the free volume notion, only limited experimental data on free volume in polymers have been reported [2,3]. One of the potentially most powerful technique for determining free volume sizes in non-conductive materials is positron annihilation lifetime spectroscopy (PALS).

PALS is capable of determining the free volume hole properties directly. This capability arises from the fact that positronium (bound state of positron and electron, Ps) is preferentially localized in regions of free volume of atomic scale. The primary mechanism of annihilation of triplet positronium (o-Ps) is by pick-off with electrons of the bulk medium. Thus the life-time of o-Ps ($\tau_3 \leq 142$ nsec) is sensitive to its local molecular environment. Generally, the lifetime of o-Ps is determined by an overlap integral between the positron and the electron densities in the hole. One expects the o-Ps lifetime to correlate directly with the hole size because a larger hole, which contains a lower mean electron density, results in a longer Ps life-time. A number of semiempirical correlations between the free volume size and the annihilation rate have been developed [4,5]. All of them are based on a simple quantum mechanical model where o-Ps resides in a spherical well having an infinite potential barrier of radius R_0 with a homogeneous electron layer in the region $R < r < R_0$ ($R_0 = R + \Delta R$). Such a model predicts a connection between τ_3 and the free volume hole size. Using this semiempirical model and a value $\Delta R = 1.656$ Å from fitting the measured τ_3 of cavities with known sizes, one can determine the average absolute size of free volume holes from the relation

$$1/\tau_3 = 2[1 - R/R_0 + (1/2\pi) \sin(2\pi R/R_0)] \quad (1)$$

where τ_3 and R are expressed in nanoseconds and Ångströms, respectively. Until recently, the analysis of positron decay curves into 3- or 4-components limited such analyses to the determination of average free-volume radius by converting the measured o-Ps lifetime (τ_3 or τ_4) according to eq.1. R. B. Gregory [3] has developed a new technique for the analysis of positron annihilation lifetime data using a Laplace transform method to obtain a continuous distribution of o-Ps lifetimes from PALS spectra.

In the present work we describe the application of Gregory's algorithm [6] to derive free-volume radius and volume distributions in polycarbonate and polyoxymethylene polymers at different temperatures.

Experimental Procedures

Disks of 10-mm diameter were machined from polycarbonate and polyoxymethylene sheets of ~ 5 mm thickness. The samples were prepared at the Polymer Institute. The positron source $^{22}\text{NaCl}$ was deposited in an envelope of KAPTON foils (8 μm thick) and then sandwiched in between two identical pieces of the samples. This sandwich was completely enclosed in a copper sample holder at the end of the cold finger of a close-cycle helium gas refrigerator. Each selected temperature was kept constant within ± 0.5 K during data acquisition. The entire source-sample assembly was placed in vacuum. The following sequence of measurements was carried out:

- a) The measurements were performed at 293 K on samples immediately after source installation.
- b) Next the temperature was lowered to ~ 50 K and then the temperature was raised to 293 K in steps of 10 K and lifetime spectra were obtained at each temperature. At least two sets of such measurements have been performed.
- c) Approximately 20 hour measurements have been carried out at 75 and 293 K, respectively.

During periods of constant temperature lifetime spectra were collected on a PC-multi-channel analyser within 60 minutes. We employed a lifetime spectrometer with plastic scintillators coupled to Philips XP2020 photomultipliers. ORTEC 583 constant fraction discriminators were used for selecting the energy and providing timing signals to a time-to-amplitude converter. With an appropriate window setting of both CDF's (511 keV and 1275 keV) spectra with 320 ps (FWHM) time resolution were obtained. A model-independent estimate of the instrument resolution function was obtained from the decay curves of ^{207}Bi isotope with a single lifetime of 182 ps. These ^{207}Bi data have been used in conventional data analysis (fit of several exponentials) as well as in the numerical Laplace transform method.

In conventional analysis the PATFIT-88 program [7] was employed. Source correction terms were subtracted from each spectrum. The resolution function was approximated as a sum of three Gaussians. Three- as well as four-component analyses of data were performed. Four-component analyses described the polyoxymethylene data very well, but the use of four components for polycarbonate gives an error for the intensity of the third component (~ 900 ps) comparable to the intensity itself.

Results

In Fig.1 the results of measurements of the o-Ps decay as a function of temperature in the amorphous polycarbonate material are displayed. Data are well described by two lines with an intercept at $T_b = 127.3 \pm 21.0$ K. We can say that τ_3 does not change below T_b .

Fig.1. Temperature behaviour of o-Ps decay (τ_3 [ns]) for amorphous polycarbonate.

Fig.2. Temperature behaviour of o-Ps decay (τ_3 [ns]) for semicrystalline polyoxymethylene.

The temperature behaviour of the semicrystalline polyoxymethylene (Fig. 2) is different. Below ~ 110 K τ_3 is a constant but above this temperature the data cannot be fitted by one line only due to a structure at ~ 160 K. Results from the PATFIT-88 program with a free-fitting procedure for both polymers at temperatures of 75 and 293 K are listed in Table 1 and 2, respectively.

Table 1. Positron lifetime results in a polycarbonate at the temperatures of 75 and 293 K, respectively

T [K]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	I_1 [%]	I_2 [%]	I_3 [%]
293	203±6	507±12	2141±10	36±2	35±2	29±1
75	201±10	453±10	1802±8	31±2	47±2	22±1

Table 2. Positron lifetime results in a polyoxymethylene at the temperatures of 75 and 293 K, respectively

T [K]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]	I_1 [%]	I_2 [%]	I_3 [%]
293	198±3	509±9	2550±10	47±1	30±1	23±1
75	187±6	439±14	1334±11	43±2	37±2	20±1

Next, we analyzed the PALS spectra taken at 293 K and 75 K as a continuous lifetime distribution using the modified CONTIN program [6,8]. Constrained, regularized least-squares solution of the Fredholm integral equation provides the positron annihilation rate probability density function $\alpha(1/\tau)$. Only that portion of $\alpha(1/\tau)$ describing the distribution of rates for o-Ps species has been considered in the derivation of the corresponding free-volume probability density distribution (PDF). The transformation of the annihilation rate PDF $\alpha(1/\tau)$ to the corresponding radius PDF for the free-volume region in which o-Ps annihilates is obtained from eq.(1). The radius PDF is given by

$$f(R) = 2\Delta R(\cos[2\pi R/(R + \Delta R)] - 1)\alpha(1/\tau)/(R + \Delta R)^2 \quad (2)$$

Then the fraction of positrons annihilating in cavities with radii between R and $R + dR$ is $f(R)dR$. The free-volume PDF assuming a spherical cavity is

$$g(V) = f(R)/4\pi R^2 \quad (3)$$

In Fig. 3 we show the results of $f(R)$ for the polycarbonate at 293 and 75 K. The free-volume PDFs, $g(V)$, calculated according to eq.(3) for data from Fig. 3 are plotted in Fig. 4. In Fig. 5 we show $f(R)$ for the polyoxymethylene sample at 293 and 75 K. Free volume PDFs $g(V)$ from the $f(R)$ results of Fig. 5 are displayed in Fig. 6.

Comparing the lifetime results obtained by using the CONTIN program and by the PATFIT-88 program, we found that results of long lifetimes, τ_3 and I_3 , agree with each other. There are discrepancies obtained in the results concerning the p-Ps. Moreover, we found that results of o-Ps lifetime distribution are stable and unique. Therefore, they can be correctly used to interpret the free-volume distribution in polymers. The mean values of R and V calculated from probability density distributions

are given in Table 3 for polycarbonate and in Table 4 for polyoxymethylene.

Fig.3. Hole radius distribution function $f(R)$ at temperatures 293 K and 75 K for amorphous polycarbonate.

Fig.5. Hole radius distribution function $f(R)$ at temperature 293 K and 75 K for semicrystalline polyoxymethylene.

Fig.4. Distribution of free volumes $g(V)$ at temperatures 293 K and 75 K for amorphous polycarbonate.

Fig.6. Distribution of free volumes $g(V)$ at temperatures 293 K and 75 K for semicrystalline polyoxymethylene.

Table 3. Mean free volume hole radius $\bar{R}$, mean free volume $\bar{V}$ and σ -width of $f(R)$ of a polycarbonate at different temperatures

T [K]	$\bar{R}$ [Å]	$\bar{V}$ [Å³]	σ [Å]
293	2.83 ± 0.02	92.4 ± 2.0	0.94
75	2.55 ± 0.05	69.5 ± 4.1	0.73

Table 4. Mean free volume hole radius $\bar{R}$, mean free volume $\bar{V}$ and σ -width of $f(R)$ of a polyoxymethylene at different temperatures

T [K]	$\bar{R}$ [Å]	$\bar{V}$ [Å³]	σ [Å]
293	3.10 ± 0.07	124.6 ± 8.0	1.37
75	2.06 ± 0.02	35.4 ± 1.2	0.58

All errors are statistical ones. They do not include possible systematic errors arising from the analysis procedure. The hole radius distribution function $f(R)$ is symmetric and can be characterised by a full width at half - maximum σ . As intuitively expected, an increase in the temperature results in an enlargement of the free-volume holes.

This increase of $\bar{R}$ is different for an amorphous polycarbonate and semi-crystalline polyoxymethylene, i. e. 11% and 50% increase, respectively. Also, the temperature behaviour of σ is different for polycarbonate and polyoxymethylene, the increase of $\sim 30\%$ and $\sim 140\%$ has been observed. Such temperature behaviour of $\bar{R}$ ($\bar{V}$) can be explained by a simple thermodynamical model [9] where holes are thermally generated and a dynamical equilibrium between creation of hole and its annihilation takes place.

Conclusions

We have presented results of positron lifetime measurements in polycarbonate and polyoxymethylene carried out at different temperatures. Positron lifetime spectra were analyzed by means of the PATFIT-88 program in a free three-component analysis and by the CONTIN program. The temperature behaviour of the free-volume hole size distribution has been deduced for an amorphous polycarbonate and a semicrystalline polyoxymethylene.

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