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DOES POSITRONIUM FEEL DYNAMICS OF POLYMER CHAIN?

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The annihilation experiments on simple elastomers at wide temperature interval of (15–370) K will be described. The results are consistently interpreted using free-volume models of polymer structure. The procedure of deducing some parameters of theory of polymers (e.g. viscosity, Vogel–Fulcher temperature) from the positron annihilation experiments will be shown. A great potential of positron annihilation in the study of amorphous polymers will be emphasized.

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1. Introduction

According to the free volume concept of mobility in disordered media [1] a given mode may be realised in certain local regions of matrix with the lowered local density only. Therefore, the knowledge of the local structure on a scale of 10^{-7} cm opens up the way to better understanding of motional mechanisms, mechanical and transport properties.

We can regard glassy amorphous polymers as consisting essentially of inter-penetrating statistical coils. This coil forms occupied volume V_0 . In general, unoccupied free volume V_f can be written as $V_f = V_t - V_0$, where V_0 is the volume occupied by the molecules at 0 K in a close-packed state and V_t is the total volume. The fraction of free volume f_V is then defined as $f_V = V_f/V_t$. We also assume that the free volume is not static but it is an open space that is freely moving in a medium [2].

In polymers and in other molecular materials a substantial fraction of the injected positrons forms positronium (Ps). The Ps is repelled by screened atomic nucleus and trapped in open spaces, such as holes and voids. Due to small size of

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Ps (1.06 Å) it is particularly sensitive to small holes in a size of Å and at a time of molecular motion from 10^{-10} s and longer.

In 1976 Tao [3] proposed a simple model in which the Ps particle resides in a spherical well with the radius R . The Ps wave function has a finite penetration depth ΔR into the material surrounding the potential well. Then *o*-Ps pick-off lifetime τ can be related to the radius of the hole R as

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

A value $\Delta R = 1.66$ Å is obtained by fitting (1) to the observed *o*-Ps lifetime of known mean hole radii in zeolites and other substances. The validity of the ΔR value is further supported by the fact that the zero-point energy of Ps atom trapped in the potential becomes equal to the binding energy of Ps (6.8 eV) as R approaches 1.66 Å [4].

Equation (1) is the foundation for the determination of mean size of free-volume hole by using positron annihilation spectroscopy. This model is very rough but its application leads to reasonable conclusions, in some cases, they have been verified by another approaches.

2. Experimental techniques and data analysis

2.1. Lifetime measurements

The positron lifetime spectra are obtained by the conventional fast-fast coincidence method. Using the ^{22}Na source of 2MBq activity about a million counts can be measured and stored within some hours. The full width at a half maximum (FWHM) of the time resolution spectrum is *ca.* 300 ps. The lifetime spectra are treated by the PATFIT-88 software package of Kirkegaard et al. [5].

The relative intensity corresponding to the longest lifetime I_3 contains information related to the number of the free-volume holes. We must stress that this point is now under hot discussion. Nevertheless, a semi-empirical equation has been proposed to determine the fraction of free volume f_V in polymers as [6] $f_V = CV_f I_3$, where V_f is the free volume obtained from τ_3 using Eq. (1), and C is a parameter which can be determined by calibration.

The lifetime spectra measured with substantially higher statistical accuracy (several millions counts) can be analysed using the Laplace inversion program CONTIN-PALS [7]. The distribution function $\lambda\alpha(\lambda)$ is calculated from the experimental positron lifetime spectrum $N(t)$ via numerical Laplace inversion including the deconvolution of the experimental resolution $R(t)$. The $R(t)$ can be obtained from decay of ^{207}Bi nucleus. The lifetime distribution may be transformed into a hole volume density distribution $g(V)$.

2.2. Doppler broadening measurements

The HPGc detector with an energy resolution of 1.6 keV for 511 keV photon is used in Doppler broadening (DB) measurements. The S -parameter is used. It is defined as the sum of counts in an energy interval around the top of the photopeak divided by the total area of the peak.

Key problem of DB measurements is a stability of electronics. Small change in energy dispersion spoils the S -parameter. This problem was partially solved in Ref. [8] where Gold iterative method of deconvolution compensated small shift in annihilation γ -ray spectrum.

3. Results

Positron lifetime and Doppler broadening measurements were carried out for set of simple elastomers having no large side groups. The basic properties of six studied samples are collected in Table I.

TABLE I

Characteristics of studied samples. PBD — poly-(butadiene), PIB — poly(isobutylene), PIP — poly(isoprene), PCIP — poly(chloroprene), a-PP — atactic poly(propylene). \bar{M}_w — molecular weight, X_c — crystallinity, T_g — glass transition temperature determined by DSC, T_{ll} — temperature of liquid-liquid transition.

Sample	\bar{M}_w	T_g [K]	T_{ll} [K]	X_c [%]
1,4-cis-PBD	8.1×10^5	168	208	19
1,2-PBD	2×10^5	272	—	—
PIB	4.2×10^5	203	263	—
1,4-cis-PIP	8×10^5	203	243	—
1,4-trans-PCIP	7×10^5	235	280	28
a-PP	1×10^5	260	303	—

Samples for measurements were in the form of discs of 10 mm diameter and *ca.* 5 mm thick. We used several positron sources with different activities, weaker *ca.* 100 kBq and stronger 2 MBq. The activity was sealed between two 8 μ m Kapton foils or 3.5 μ m Ni foils (2 MBq). All samples were studied at wide temperature interval, from 14 K up to 350 K and more. The source-sample assembly was kept in rotary pump vacuum. The high temperature measurements (up to 470 K) were performed in normal air atmosphere. During all measurements an automatic temperature regulation was used.

Several different ways of cooling and heating of samples were used. One so-called "heating" was fast cooling to 14 K with the cooling rate of 4 K/min. The second regime, so-called cooling, was slow cooling of samples from room temperature to 14 K. The cooling rate is estimated to be 0.5 K/min.

Positron lifetime spectra were then measured as a function of increasing (decreasing) temperature with temperature step of 5 or 20 K.

The Doppler broadening of annihilation line was measured simultaneously with the lifetime measurement.

A part of obtained temperature dependencies of τ_3 , I_3 and S -parameter is shown in Fig. 1 for poly(isobutylene). The sum of our results concerning τ_3 dependence on temperature is displayed in Fig. 2. In this case we used the glass transition temperature T_g as a scaling parameter. These figures show typical

behaviour of *ortho*-positronium lifetime with abrupt change of slope at the glass transition temperature T_g . In all samples we observed similar behaviour. Some differences were seen at higher temperatures. We observe a constant value of τ_3 in PCIP and 1,4 PBD samples at the temperature $T \approx 1.3-1.5T_g$.

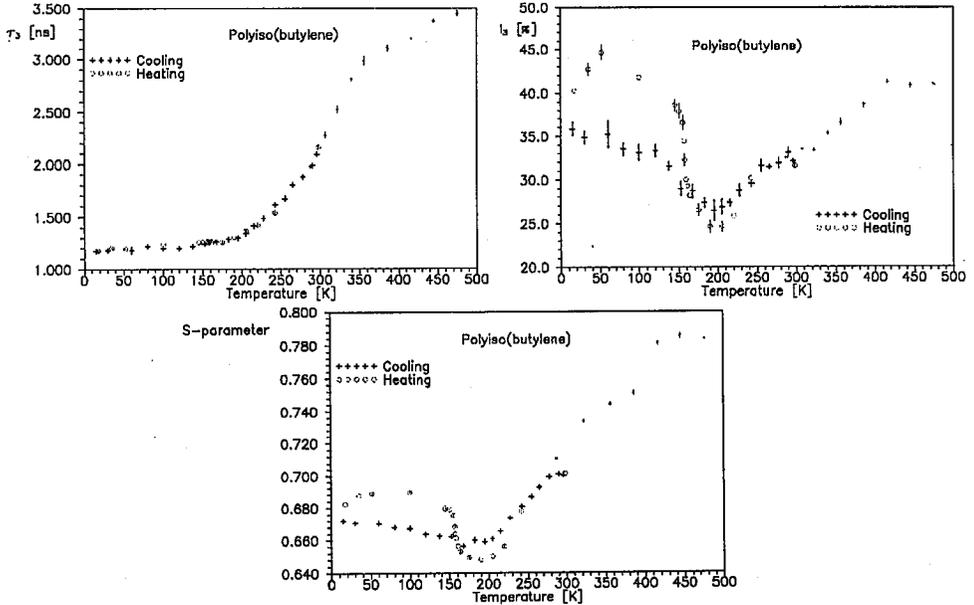


Fig. 1. The temperature dependence of positron annihilation parameters τ_3 , I_3 , and S in poly(isobutylene).

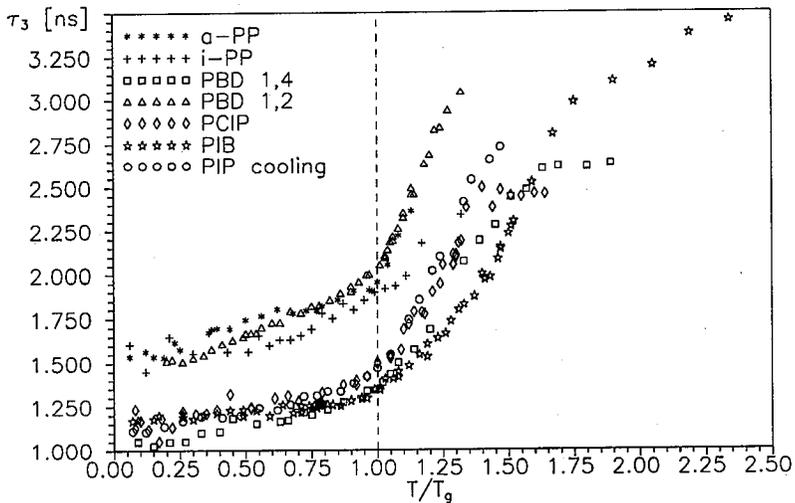


Fig. 2. The temperature dependence of τ_3 , T_g -glass transition temperature.

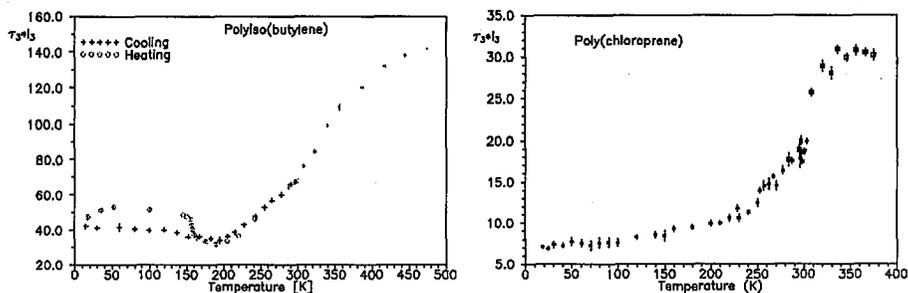


Fig. 3. The temperature behaviour of free volume fraction f_V of poly(isobutylene) and poly(chloroprene).

The course of the intensity of the third component is more complicated especially for PIP and PIB samples.

In Fig. 3 we present temperature behaviour of the free-volume fraction f_V of PIP and PCIP. In the case of PIB and PBD we observed that I_3 depends on a cooling rate during the measurements [9]. The I_3 is higher when the cooling rate is 4 K/min in comparison with the rate of 0.4 K/min. Such behaviour is consistent with non-ergodic behaviour of glassy state and it is indirect argument in favour of using positronium as a detector ("seeker") of free-volume holes.

In Fig. 3 the increase in f_V with temperature indicates the thermal expansion of free-volume hole or Ps cavity. Each curve can be approximated by neighbouring lines with a slope that can provide a value of thermal expansion coefficient of free volume α_f felt by positronium atom. All slopes are normalised to the value of f_V at T_g . The mean size of the free volume holes was calculated from the mean lifetime τ_3 with help of semiempirical relation (1). Then the thermal expansion coefficient of hole α_h can also be calculated.

TABLE II

The thermal expansion coefficients of α_h [K^{-1}] and α_V [K^{-1}].

Sample	$\alpha_h (T < T_g)$ $\times 10^3$	$\alpha_h (T > T_g)$ $\times 10^2$	$\alpha_V (T < T_g)$ $\times 10^4$	$\alpha_V (T > T_g)$ $\times 10^4$
1,4-cis-PBD	3.7	3.1 ± 0.9	1.9	7.5
1,2-PBD	—	1.4 ± 0.2	—	6.1
PIB	1.2	1.9 ± 0.3	1.4	5.7
1,4-cis-PIP	1.9	1.6 ± 0.2	1.9	5.8
1,4-trans-PCIP	2.1	2.0 ± 0.4	—	6.1
a-PP	1.5	1.4 ± 0.2	1.9	7.1

In Table II the values of α_h are summarized together with available data on the macroscopic thermal expansion coefficient α_V determined by dilatometry [10, 11]. The data stress the need to find an explanation of systematic and almost two order difference between α_h and α_V .

The published simple model [12] is able to explain the values of α_f .

A new model of free volume expansion was proposed [13]. The basic volume-temperature relations of model is depicted in Fig. 4. The occupied volume is expanding with the expansion coefficient α_{01} . Thus

$$V_0(T) = V_0(T_g)[1 + \alpha_{01}(T_g)(T - T_g)]$$

and

$$V(T) = V(T_g)[1 + \alpha_V(T_g)(T - T_g)].$$

Algebraic manipulations give the expressions for the expansion coefficients of free volume

$$\begin{aligned} T < T_g, \quad \alpha_{V_{i_1}}(T_g) &= \frac{\alpha_1(T_g) + \alpha_{01}(T_g)[f_V(T_g) - 1]}{f_V(T_g)} \\ T > T_g \quad \alpha_{V_{i_2}}(T_g) &= \frac{\alpha_2(T_g) + \alpha_{01}(T_g)[f_V(T_g) - 1]}{f_V(T_g)}. \end{aligned} \quad (2)$$

We can solve Eq. (2) to obtain the following relations for parameters, the expansion of occupied volume $\alpha_{01}(T_g)$ and the free-volume fraction at T_g , $f_V(T_g)$:

$$\alpha_{01}(T_g) = \frac{\alpha_2(T_g)\alpha_{V_{i_1}}(T_g) - \alpha_1(T_g)\alpha_{V_{i_2}}(T_g)}{[\alpha_2(T_g) - \alpha_1(T_g)] - [\alpha_{V_{i_2}}(T_g) - \alpha_{V_{i_1}}(T_g)]}$$

and

$$f_V(T_g) = \frac{\alpha_2(T_g) - \alpha_1(T_g)}{\alpha_{V_{i_2}}(T_g) - \alpha_{V_{i_1}}(T_g)}. \quad (3)$$

Very important conclusions follow from our approach:

— the combination of macroscopic dilatometric and microscopic positron annihilation data provides quantitative information on the free-volume fraction, f_V ,

— there is a possibility to determine the temperature T_∞ in which a change of free-volume entities begins, i.e. $V_f(T_\infty) = 0$, $T_\infty = T_g - 1/\alpha_{V_{i_2}}(T_g)$.

In Table III the calculated parameters $\alpha_{01}(T_g)$, $f_V(T_g)$ and T_∞ are summarized. The values of Vogel-Fulcher temperature T_0 determined by relaxation,

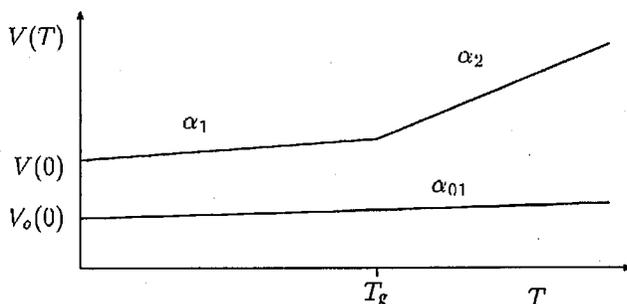


Fig. 4. The temperature behaviour of total volume $V(T)$, α_i are thermal expansion coefficients, α_{01} is thermal expansion coefficient of occupied volume.

TABLE III

The parameters of free volume calculated from model [13].

Polymer	$\alpha_{01}(T_g)$ $\times 10^4$	$f_V(T_g)$	T_∞ [K]	T_0 [K]	T_f [K]
1,4-cis-PIP	1.39	0.029	132	134	—
PIB	1.24	0.024	145	112	140
1,4-cis-PBD	1.35	0.020	134	117	120±7
a-PP	1.14	0.042	189	192.5	190
1,4-trans-PCIP	1.85	0.021	180	—	180 ± 10

Typical errors: $\alpha_{01}(T_g) \pm 0.03$, $f_V(T_g) \pm 0.001$, $T_\infty \pm 3$.

NMR or viscosity measurements [14–16] are given for comparison. The temperature T_f , in which the fast process observed by quasielastic neutron scattering starts to appear, is also displayed.

Correlation among T_0 , T_f and T_∞ is worthy noting. Recent neutron scattering experiments [17–19] on the microscopic dynamics below and above the glass transition temperature T_g provide the Debye–Waller factor e^{2W} , $W = Q^2 \langle r^2 \rangle / 6$, where Q is the momentum transfer of neutron and $\langle r^2 \rangle$ is the mean squared displacement of scatterer. The temperature behaviour of $\langle r^2 \rangle$ is linear below as well as above T_g . The relative slopes of $\langle r^2 \rangle$ (the expansion coefficient of $\langle r^2 \rangle$) have been calculated. They are summarized in Table IV.

The comparison of Table II and IV shows remarkable resemblance of the rate of change of two geometrical quantities (α_h and $\alpha(\langle r^2 \rangle)$) with temperature.

TABLE IV

The rate of change of the mean squared displacement $\langle r^2 \rangle$ with temperature T .

	$\alpha[\langle r^2 \rangle]$ [K ⁻¹]	
	$T < T_g$	$T > T_g$
1,4-PBD	5.9×10^{-3}	3.7×10^{-2}
PIB	4.9×10^{-3}	5.5×10^{-2}
PCIP	4.5×10^{-3}	1.8×10^{-2}
a-PP	3.9×10^{-3}	3.1×10^{-2}

It was said that dynamical properties and consequently, various physical and physico-chemical ones are determined not only by the mean free-volume hole size and its concentration but also by the free-volume hole size distribution. Figure 5 shows an example of dependence of the free-volume hole distribution on temperature for a typical amorphous polymer — PIB as obtained using CON-

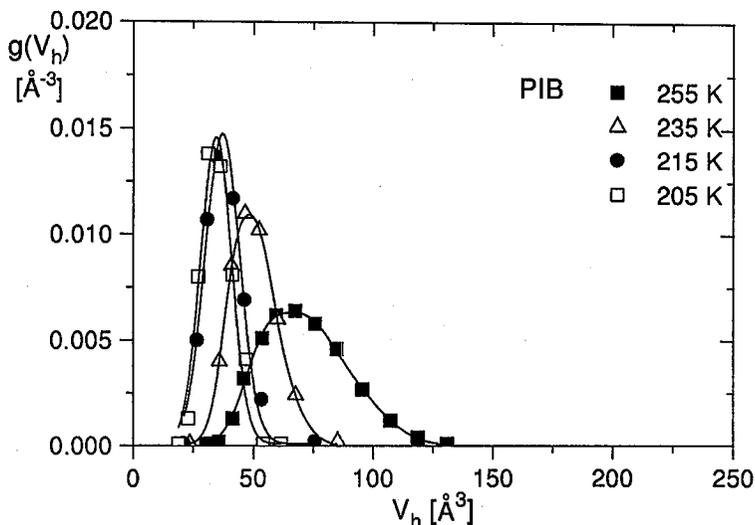


Fig. 5. Free volume distribution $g(V_h)$ of poly(isobutylene) at the temperature 205, 215, 235, 255 K.

TIN programme. Qualitatively, the maxima of distributions shift to higher values with increasing temperature. Simultaneously, widening of distribution occurs, which is small in lower temperature range and pronounced at higher temperatures, especially well above T_g . Analogical trends were observed in other elastomer cis-1,4-poly(butadiene) [20].

4. Conclusion

We have discussed our most recent results on probing the free volume in polymers by means of positron annihilation lifetime (PAL) spectroscopy. We found many encouraging correlations between results of positron annihilation, quasielastic neutron scattering and more traditional methods (viscosity, NMR and so on). We have formulated the hypothesis explaining up to two order difference in the expansion of the bulk substance and the microscopic free volume.

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