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Effect of Temperature on the Free Volume in Glassy Poly(ethylene terephthalate)

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ABSTRACT: Positron annihilation lifetime measurements have been carried out for glassy poly(ethylene terephthalate) (PET) as a function of temperature in the temperature range from 15 to 300 K. The structural relaxation and transition were studied by positron annihilation lifetime spectroscopy (PALS). According to the variation of orthopositronium(o-Ps) lifetime with temperature, two intercept temperatures were observed and were designated as the secondary transition temperatures T_γ (γ transition) and T_β (β transition). The coefficient of thermal expansion of the free volume hole was estimated from the temperature dependence of the free volume. We found that the size of free volume holes does not change significantly with temperature when $T < T_\gamma$, and that it increases evidently with temperature above T_γ. On the other hand, the distribution of the free volume was examined by developed maximum entropy lifetime method (MELT). Continuous analysis clearly indicated that the free volume distributions were broadened and that the value of peak was shifted toward high value with increasing temperature.

Introduction

The relationship between microstructure and physics properties of polymers is an interesting tropic in polymer science. The structural characterization of polymers is very important for understanding and improving their properties. On the other hand, the secondary relaxation for polymers is still unclear except for polyethylene.[1] It is well-known that the local free volume holes in structurally disordered polymers play a crucial role in determining its physical properties, such as the mechanical properties and diffusion phenomena. The average free volume hole size, size distribution, and content influence the relaxation spectra, mobility of segments, and various transport phenomena in polymers.[2,3] Precious measurement of the free volume parameters, in particular the free volume distribution in polymers, becomes necessary to provide structural information that related to the bulk properties of polymers.

Although a great deal of research effort was expended in the past decade toward understanding the influence of free volume on the physical properties of polymers, only limited information with regard to free volume size, concentration, and shape has been forthcoming. In fact, reports of direct experimental measurement of these parameters are essentially nonexistent.[4−6] For studying the size distributions of the free volume holes experimentally, PALS proved to be a sensitive tool. PALS has been widely used to study the microstructure of polymers. Recently, Shukla et al. has developed a program named the maximum entropy method (MELT), in which the maximum entropy method of resolution is applied.[7,8] It has been shown that MELT is a promising method for finding a reliable o-Ps distribution of a positron lifetime spectrum in polymers.[9−13]

The aim of the present study is to investigate the effect of temperature on the microstructure in glassy PET. In this paper, the size, the concentration and distribution of the free volume hole were examined in the low-temperature range from 15 to 300 K using PATFIT and MELT. The structural transition and the secondary relaxation were studied.

Experiments

An amorphous PET sample (molecular weight 39 000) was heated to 370 K above its glass transition temperature T_g (340 K) determined by differential scanning calorimeter (DSC) for 15 min, to erase any previous thermomechanical history prior to the positron lifetime measurements, and then cooled to room temperature by immersing in water. Positron lifetime spectra were measured using a fast−fast coincidence spectrometer. The time resolution of the system was found to be a sum of two Gaussian with $(\text{fwhm})_1 = 280$ ps (91%), and (fwhm) = 260 ps (9%). A 30 μCi ^{22}Na positron source was sandwiched between two pieces of identical samples and mounted to a cryostat cooled by liquid helium for measurements of temperature dependence of positron lifetime. Each spectrum contained approximately 10^6 and 4×10^6 counts for PATFIT[14] and MELT, respectively.

Results and Discussion

1. Discrete Term Analysis and Secondary Relaxation Transition. The measured positron lifetime spectra have been well resolved into three components using PATFIT after the background and positron source correction were subtracted. As it is well-known, the third component (the longest-lived component) is assigned to the o-Ps pick-off annihilation in the free volume holes in the amorphous phase. Because only the o-Ps component is significantly sensitive to the change in the microstructure of the amorphous region, the main attention in this paper is paid to the variations of o-Ps annihilating parameters.

The temperature dependence of the o-Ps lifetime τ_3 is shown in Figure 1. It is clear that the o-Ps lifetime increases with increasing temperature, which demonstrates an increase of the free volume size with temperature because there is a relation between the o-Ps lifetime and radius of the free volume hole as follows[15]

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \qquad (1)$$

where R is the radius of the free volume hole, $\Delta R = 1.656$ Å derived from fitting the observed o-Ps lifetimes in molecular solids with known hole sizes. However,

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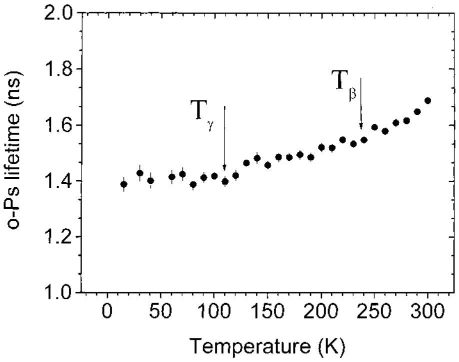

Figure 1. Temperature dependence of o-Ps lifetime.

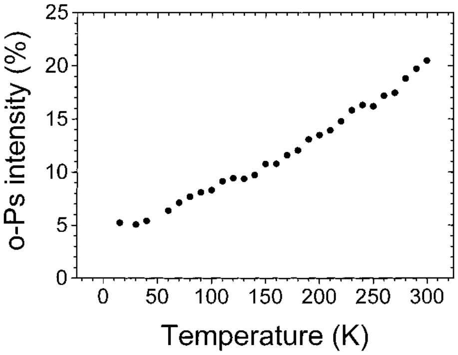

Figure 2. Temperature dependence of o-Ps intensity.

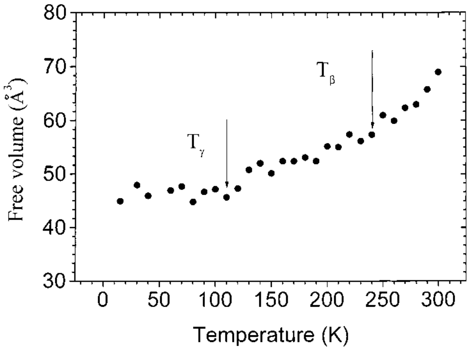

Figure 3. Temperature dependence of free volume hole.

Table 1. Average Thermal Expansion Coefficient of the Free Volume Holes

temp interval (K)	$15 \le T < 110$	$120 \le T < 240$	$250 \le T < 300$
α (Å^3/ K)	7.19×10^{-4}	7.07×10^{-2}	1.65×10^{-1}

the slope $d\tau_3/dT$ is obviously different in different temperature ranges, indicating the existence of structural transitions. To determine the structural transition temperature, a least-squares linearly fitting of straight was used to approximate the temperature dependence of the o-Ps lifetime. An empirical relation between o-Ps lifetime and temperature can be linearly fitted within three temperature regions as follows:

$$\tau_3(T) = 1.4125 + 8.8217 \times 10^{-5} T \text{ (ns)} \quad (2)$$

$$(15 \le T \le 110 \text{ K})$$

$$\tau_3(T) = 1.3238 + 9.6991 \times 10^{-4} T \text{ (ns)} \quad (3)$$

$$(120 \le T \le 230 \text{ K})$$

$$\tau_3(T) = 1.0794 + 1.9802 \times 10^{-3} T \text{ (ns)} \quad (4)$$

$$(240 \le T \le 300 \text{ K})$$

Combining eqs 2 and 3 gives the crossing point at 110 K, which is identified as the γ transition temperature T_γ related to the small segmental motion, such as the crankshaft motion of CH_2 groups or the rotation of small parts of the molecules containing several C−C links.[16] Below T_γ, τ_3 has little increase because the segmental motion is frozen by the van der Waals forces among the chains, only small fluctuations are allowed and the free space around the chains is small: any increase of temperature produces small effects on the thermal motion of the polymer chains. Therefore, small variations of τ_3 vs temperature must be expected. So the expansion of the free volume holes is neglected(see below). Although the o-Ps lifetime is nearly constant, the o-Ps intensity increases obviously with temperature as shown in Figure 2. Such a phenomenon has been found in several polymers.[17−20] A possible explanation is that the“ fast motion” that has a localized and cage character[21] is frozen, which meant that the o-Ps has a greater chance of being localized in free volume holes. The γ-relaxation is a composite relaxation because it involves not only defects in crystals but also molecules in the amorphous regions.[1] Our experimental results provide some information value for understanding γ-relaxation of PET. Another crossing point at 240 K can be derived in terms of eqs 3 and 4, which has been identified as the β transition temperature and assigned only tentatively either to the motion of chain ends or to some restricted motion of the main chain.[22−23] This result agrees well with the report in the literature.[24] When $T > T_\gamma$, this “fast motion” may be activated with increase of temperature and the local segmental motion can occur, therefore, the ends and the separation of the local segmental motion occur, which results in increase of the free volume number. At the same time, the higher the temperature, the bigger the free volume hole. The competing result of these courses brings about an increase in free volume.

The variation of the o-Ps lifetime τ_3 with temperature reflects the thermal expansion of the average size of free volume holes in which o-Ps becomes localized. A direct estimation of the thermal expansion coefficient, α, of hole volume can be made from the assumed linear relation

$$V_g(T) = V_g(0) + \alpha(T)T \quad (5)$$

where $V = 4\pi R^3/3$, R is directly calculated using eq 1, and $V_g(0)$ is the hole volume at $T = 0$ K, where the subscript g means the glassy state. The temperature dependence of the free volume hole size is plotted in Figure 3. In Figure 3, we can see that the change in the free volume hole is very small below T_γ. The small size of free volume holes indicates a very effective packing of the chains. However, we observe the pronounced increase of the free volume hole when $T > T_\gamma$. This fact means that the thermal expansion of the free volume hole is extremely marked. The values of α in different temperature regions are listed in Table 1.

From Table 1, it can be seen that the change in size of the free volume hole is rather small when $T < T_\gamma$ and that the increase in the average thermal expansion coefficient of the free volume hole with increase of temperature is very marked when $T > T_\gamma$. Thus, the local segmental motion can occur due to the thermal

Table 2. o-Ps Annihilation Parameters at Several Representative Temperatures Obtained by PATFIT and MELT

	T (K)	30	60	100	150	210	250	300
PATFIT	τ_3 (ns)	1.4284 ± 0.03	1.4149 ± 0.02661	1.4183 ± 0.0211	1.4578 ± 0.017	1.5199 ± 0.016	1.5934 ± 0.0154	1.6886 ± 0.013
	I_3 (%)	5.1 ± 0.18	6.38 ± 0.21	8.3 ± 0.2	10.8 ± 0.2	13.96 ± 0.3	16.20 ± 0.26	20.5 ± 0.3
MELT	τ_3 (ns)	1.4237	1.4503	1.4273	1.4329	1.5102	1.5887	1.6881
	I_3 (%)	5.0	6.0	8.1	10.8	13.9	16.1	20.4

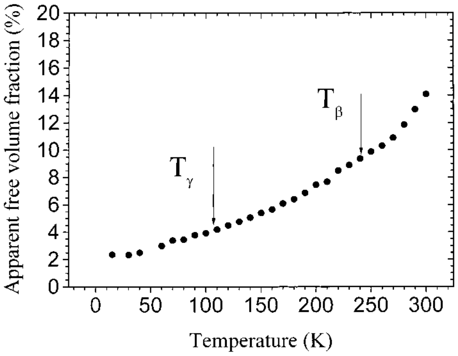

Figure 4. Temperature dependence of the apparent free volume.

Table 3. Thermal Coefficient α_I for the o-Ps Intensity

temp interval (K)	$15 \le T < 110$	$120 \le T < 240$	$250 \le T < 300$
α_i (K^{-1})	4.48×10^{-2}	6.59×10^{-2}	8.65×10^{-2}

expansion of the free volume providing the motional space.

On the other hand, the apparent free volume fraction (f_{app}) was evaluated using

$$f_{app} = VI_3 \tag{6}$$

where V is the free volume. f_{app} works as a good parameter connected to free volume fraction since the absolute value of free volume fraction is not our concern but instead the variation of free volume fraction. The variation of apparent free volume fraction is shown in Figure 4. It is clear that the apparent free volume fraction shows a continuous increase, which results from the increasing temperature. Because the thermal energy is attributed either to increase the volume of holes, or to overcome the van der Waals forces and create new holes. To examine detailed the variation of apparent free volume, empirical relation between o-Ps intensity and temperature can be linearly fitted with three temperature regions as follows:

$$I_3(T) = I_3(0) + \alpha_i(T)T \tag{7}$$

where $I_3(0)$ is the o-Ps intensity at $T = 0$ K. The values of α_i in different temperature regions are listed in Table 3. Comparing Table 1 with Table 3, we find that the increase of apparent free volume results mainly from increasing o-Ps intensity due to "fast motion" frozen, which means that there are many intrinsic free volume holes in PET when $T < T_\gamma$, and that the increase in temperature is attributed mainly to increase the volume of the holes and not their number, which also brings about the increase of apparent free volume when $T > T_\beta$.

2. Continuous Term Analysis and Free Volume Distribution. The PALS measured have been evaluated using MELT program to give continuous lifetime distribution. The positron lifetime distributions are plotted in Figure 5 at different temperatures. From Figure 5, three peaks are observed for each lifetime spectrum. We find that the values of peaks show little change for shorter lifetime components at different temperatures, but the variations of the longest lifetimes are quite explicit. For the longest lived-component, the values of peaks analyzed by MELT are consistent with the results analyzed by PATFIT as shown in Table 2.

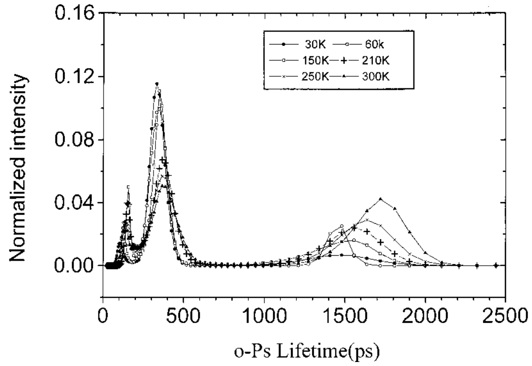

Figure 5. Positron lifetime distributions at different temperatures.

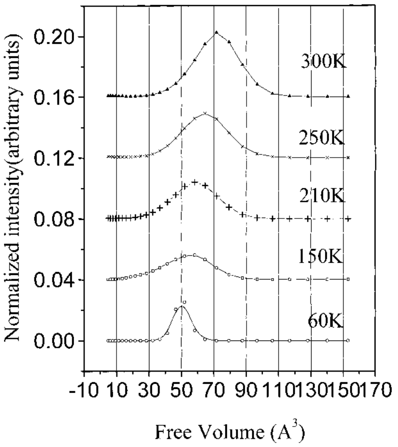

Figure 6. Free volume holes distribution at different temperatures. For clarity, the vertical ordinates are moved by 0.04, 0.08, 0.12, and 0.16.

From Figure 5, the following observations can be made: (i) the value of peak shifts to high value as the temperature is raised; (ii) the width of o-Ps lifetime distribution is widened. Figure 6 shows the free volume hole size distributions at several temperatures. The change in distribution from low temperature to high temperature can be observed. Qualitatively, the maximum of distributions shift to higher values with a rise in temperature, which suggests that the thermal expansion of the free volume holes play an important role. Below T_γ, the distribution of hole size is quite narrow, and then the distribution width increases with temperature. As mentioned above, we can say that not only the mean hole size but also the width of hole size distribution indicates a very effective arrangement of chains in the glassy polymer, because the segmental motion depends on the temperature strongly. Combining Figures 5 and 6, we may be able to conclude that T_γ is also indicating temperature at which there is a dramatic change of the width of free volume distribution.

Conclusion

The positron annihilation parameters were measured in the temperature range from 15 to 300 K for PET. Two secondary relaxation transitions were determined in the light of the variation in o-Ps lifetime with temperature, which relates to the local segmental motion. The free volume distributions were examined using recently introduced MELT program. The experimental results reveal that the size, the concentration, and the distribution of the free volume hole depend on the temperature strongly. The distribution width of the free volume hole increases with temperature. Below T_γ, the size and the distribution width are nearly unchanged. Above T_γ, the thermal expansion of the free volume is quite remarkable and the distributions of the free volume holes are widened. As mentioned above, we conclude that although polymer PET is in the glassy state, the free volume parameters are still changed. The local motions of chains can occur due to the free volume thermal expansion. This experimental result also gives information about T_γ at which there is a dramatic change of the width of free volume distribution. Thus, not only the mean hole size but also the width parameter of hole size distribution indicates a very effective arrangement of chains in the glassy state.

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