

# Detection of Glass Transition in Poly(ethylene terephthalate) and Nylon-6 by Positron Annihilation

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## SYNOPSIS

Positron annihilation lifetime spectroscopy (PALS) was used to investigate the phase transitions, mainly the glass transition, of poly(ethylene terephthalate) (PET) and nylon-6 during the thermal treatment of these polymers. The longest-lived component lifetime and intensity, indicative of *ortho*-positronium pick-off, exhibit thermal dependencies that can be attributed to the free-volume changes associated with structural transitions. Glass transition temperatures and the volume of intermolecular-space holes among polymer chains were obtained from the lifetime,  $\tau_3$ , and intensity of formation,  $I_3$ , of the long-lived component of *ortho*-positronium. For PET, the free-volume fraction and thermal expansion coefficients related to the free-volume fraction were also obtained. Double glass transition behavior was noted in the analyzed polymers, which was consistent with their semicrystalline nature as revealed by differential scanning calorimetry. Increases in the slope of the lifetime-temperature plots for nylon-6 and PET were interpreted to suggest that glass transitions are followed by an increased free-volume cavity expansion as temperature is increased. The intensity response for PET was consistent with the association of glass transition with the reduction of crystalline constraint on segmental mobility in the amorphous phase. In contrast, the intensity behavior during the thermal treatment of nylon-6 seems to be governed more by the electronic effects occurring when the polymer chains acquire mobility than by free-volume changes. Since the sensitivity of PALS is in the order of nanometers, it is expected to give an alternative novel technique to estimate phase transitions and relaxations in polymers from the point of view of the free volume.

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## INTRODUCTION

Positron annihilation lifetime spectroscopy (PALS) is an atomic level probing technique that has been shown to be extremely sensitive to vacancy-type defects in a wide variety of solids. In amorphous and semicrystalline polymers, this technique is uniquely sensitive to the free volume-based structural changes such as the glass transition.<sup>1-3</sup>

PALS of glassy polymers can normally be resolved into three and sometimes four components in the form of decaying exponential functions.<sup>1</sup> Associated with each component is a decay rate con-

stant,  $\lambda_i$ , whose reciprocal is referred to as the lifetime,  $\tau_i = 1/\lambda_i$ , and a corresponding intensity,  $I_i$ . In the case of a three-component fit, the short-lived component is associated with *para*-positronium (*p*-Ps) decay and has a mean lifetime of 0.125 ns. The intermediate component corresponds to annihilation events involving positrons in the free state and usually exhibits a mean lifetime ranging from 0.5 to 0.8 ns. Some studies have considered the inclusion of the intermediate component of *o*-Ps in ordered regions in polymers.<sup>4</sup> Most significant for evaluating free volume-based structural transitions is the longest-lived component, which is attributed to the pick-off decay of the *ortho*-positronium (*o*-Ps) component. Once formed, *o*-Ps diffuses through the material and tends to localize in regions of reduced

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density, such as free-volume sites. When localized or trapped, the pick-off annihilation rate is proportional to the local electron density, and, thus, the *o*-Ps pick-off lifetime provides information regarding the mean size of the localization sites. In addition, the corresponding intensity of the *o*-Ps pick-off component is indicative of both the Ps formation probability and the density of localization sites. Therefore, the lifetime and intensity of the *o*-Ps pick-off component is sensitive to a number of polymer properties that affect or are affected by the free volume, including phase transitions, degree of crystallinity, molecular weight, degree of crosslinking, and density.<sup>2,5-7</sup> More details of PALS are given elsewhere.<sup>8,9</sup>

In this work, commercial samples of nylon-6 and PET were heated and their transitions were detected by PALS. Double glass transition temperatures were obtained for both polymers, and a loss of crystallinity was also found for nylon-6. In addition, PALS measurements were applied to study the characteristics of these polymers from the point of view of free volume, obtaining, for PET, the mean size of free volume, the free-volume fraction, and the thermal expansion coefficients regarding the free-volume fraction, before and during its glass transition.

## EXPERIMENTAL

The materials examined in this study were commercial nylon-6 ( $\overline{M}_n = 114,000$ ) obtained in powder form from the Nylamid Co. and poly(ethylene terephthalate) (PET) ( $\overline{M}_n = 16,800$ ) obtained in pellet form from the Celanese Co.

Prior to sample fabrication, the nylon-6 powder was desiccated under vacuum to drive off any residual moisture. For nylon-6, each sample set consisted of approximately 1 g of the polymer inside a glass tube. For PET, it was necessary to melt the pellets and samples of rectangular shape ( $5 \times 10 \times 2$  mm). Samples were cut out. They were kept at room temperature for 2 days to allow for the polymer chains to become stable by aging. The <sup>22</sup>Na positron source consisted of about 20  $\mu$ Ci of <sup>22</sup>NaCl (Amersham) deposited between two thin pieces of nickel foil, and it was situated in the middle of the polymer. The sample was degassed using a vacuum pump.

Positron lifetime measurements were performed using an EG&G Ortec standard fast-fast coincidence system. Timing resolution was determined using the prompt curve arising from a <sup>60</sup>Co source with the energy windows adjusted for <sup>22</sup>Na events. In this configuration, the time resolution was 344 ps. Sam-

ple temperatures were controlled to within 0.1°C using a Brookfield EX-200 circulating bath. Three spectra were collected at each temperature, each consisting of a peak height of approximately 250,000 counts. A typical positron lifetime spectrum in a PET sample is shown in Figure 1. A positron lifetime spectrum reveals a function containing multiexponentials:

$$N(t) = \sum_{i=1,n} I_i e^{-\lambda_i t} \quad (1)$$

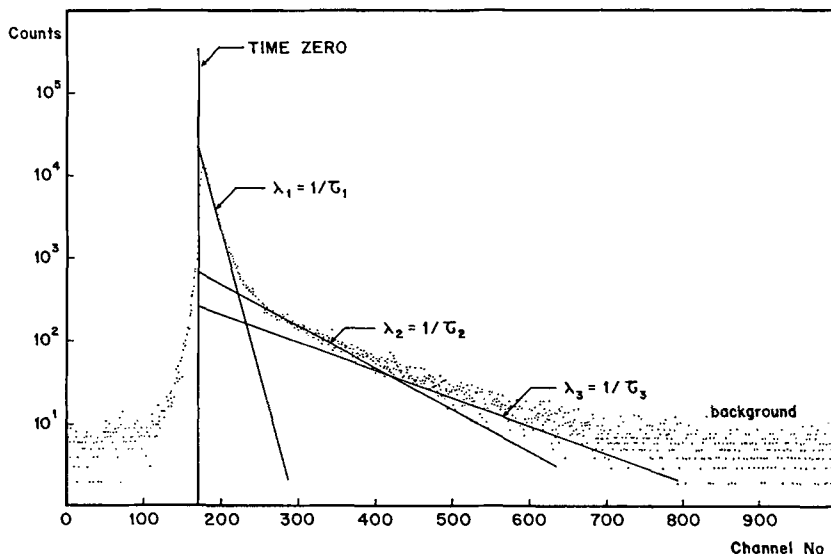
where  $n$  is the number of exponential terms,  $I_i$  and  $\lambda_i$  represent the number of positrons (intensity) and the positron annihilation rate, respectively, for the annihilation from the  $i$ th state. The positron annihilation rate is the reciprocal of the positron lifetime ( $\tau_i$ ). In most cases, one selects a finite number of positron states with a sound physical rationale and assigns an  $n$  value to fit a PALS spectrum. The resulting lifetime spectra were consistently modeled with a three-component fit, i.e.,  $n = 3$  in Eq. (1), using the computer program PATFIT.<sup>10</sup> The crystallinity percentage for nylon-6 and PET was obtained using a Perkin-Elmer DSC-7 and by following the technique already reported.<sup>11</sup>

## RESULTS AND DISCUSSION

The lifetime and intensities of the first two exponentials of the three component fit did not change appreciably as a function of temperature for any of the samples studied. However, the parameters associated with the long-lived component exhibited significant changes with temperature and will, therefore, be the subject of the remainder of this article. In the analysis, the fitting errors of the first ( $I_1$ ) and the second ( $I_2$ ) components were around 6%, while those of the third component ( $I_3$ ) were around 0.5%. Also, the fitting errors of  $\tau_1$  and  $\tau_2$  were larger than those of  $\tau_3$ , which was about 0.04 ns.

To more accurately define the glass transition temperature,  $T_g$ , and other transitions, for both samples as revealed by PALS, a linear regression analysis was used to fit two straight-line segments to the lifetime and intensity vs. temperature data. The correlation coefficient was about .96 for the segments.

*o*-Ps lifetime,  $\tau_3$ , values were plotted against the temperature applied to the nylon-6 sample. The resultant graph is shown in Figure 2, in which three discontinuities can be distinguished through the

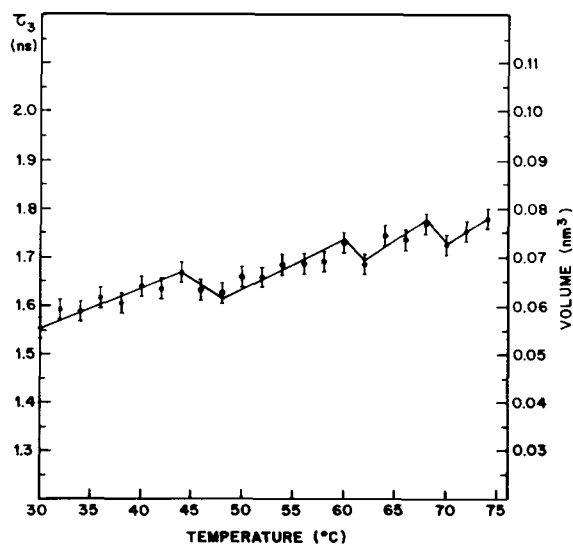


**Figure 1** Typical PA lifetime spectra taken at 75°C for PET. A standard three-component fit is depicted.

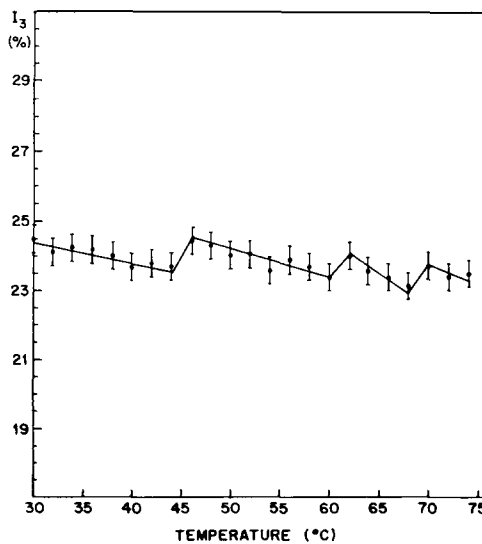
temperature range analyzed. All the graphs show the corresponding confidence intervals related to the average of the three measures performed at each temperature. Initially,  $\tau_3$  tends to decrease until 44°C, where a change in the slope occurs; this temperature can be attributed to the lower glass transition temperature [ $T_{g(L)}$ ]. After 48°C, as the temperature increases,  $\tau_3$  values augment until they reach a range between 60 and 62°C, which can be assigned to the upper glass transition [ $T_{g(U)}$ ]. Finally, and following the behavior of the curve,  $\tau_3$  continues increasing and the slope change again be-

tween 68 and 70°C. This last discontinuity might be attributable to a lost of crystallinity (“premelting”), represented by  $T_c$ .<sup>12</sup>

The behavior of the *o*-Ps intensity of formation,  $I_3$ , with respect to the thermal treatment in nylon-6 is shown in Figure 3. In general,  $I_3$  has a light diminution as a temperature augment; in addition, the same discontinuities in the curve as those in lifetime vs. temperature plot (Fig. 2) can be identified at the same temperature intervals.



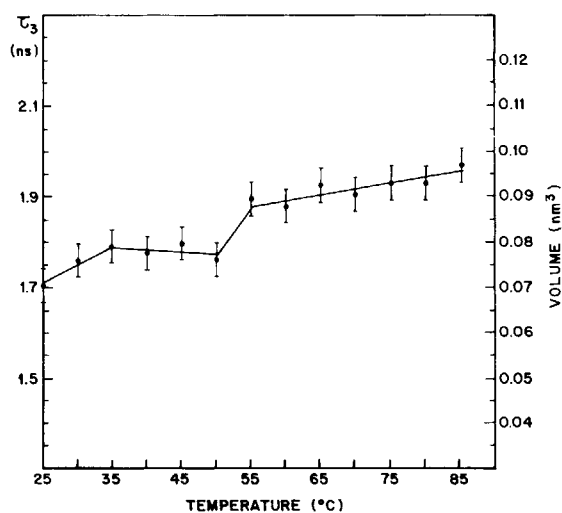
**Figure 2** *o*-Ps lifetimes and free-volume mean sizes in nylon-6 as a function of applied temperature.



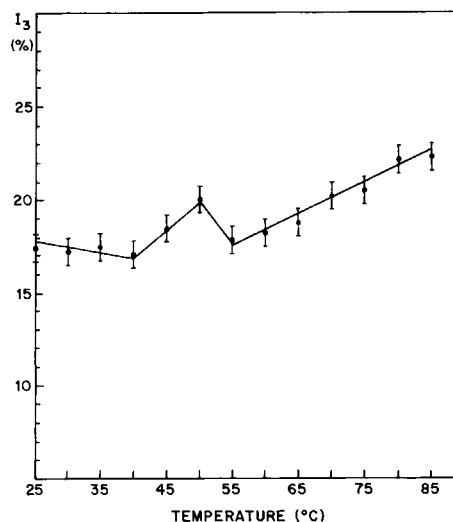
**Figure 3** *o*-Ps intensity in nylon-6 as a function of applied temperature.

During the thermal treatment of PET in the temperature range of 25–85°C, two transitions were obtained, which were detected by both *o*-Ps parameters: lifetime and intensity of formation. Results for  $\tau_3$  are displayed in Figure 4 and for  $I_3$  in Figure 5. Regarding  $\tau_3$  vs. the temperature graph,  $T_{g(L)}$  is appreciable at 35°C, the temperature at which the slope changes. After this,  $\tau_3$  showed a light diminution until it reached a temperature range between 50 and 55°C, which can be assigned to  $T_{g(U)}$ . From this last temperature,  $\tau_3$  shows a constant increase. In Figure 5, it can be observed that  $I_3$  has a first intersection at 40°C, which can be attributed to  $T_{g(L)}$  and, later, as temperature is increased, a second discontinuity appears in the temperature range between 50 and 55°C, which is ascribed to  $T_{g(U)}$ . Above the last transition,  $I_3$  still increases.

The transition temperatures detected for nylon-6 and PET by PALS are lower than those reported in the literature.<sup>13</sup> These differences are more drastic for PET, since nylon-6  $T_g$  values are more in accord with the values already reported. One plausible explanation of this deviation can be attributed to the high sensitivity of PALS, since the  $T_g$  detected by other techniques (DSC, TMA, etc.) might be related to the movement of large polymer chains and segments required for the expansion of the bulk and that the  $T_g$  perceived by PALS corresponds to that obtained from the expansion of intermolecular-space holes which requires the movement of a small part of the polymer chains surrounding the hole.<sup>14</sup> This interpretation is supported by other studies, using PALS, realized in novolac epoxy resins,<sup>14</sup> where, in one of this kind of resin, a difference of 29°C, below



**Figure 4** *o*-Ps lifetimes and free-volume mean sizes in PET as a function of applied temperature.



**Figure 5** *o*-Ps intensity in PET as a function of applied temperature.

of the  $T_g$  determined by TMA, was found using PALS. Also, for polypropylene,<sup>5</sup> a comparison concerning the variations of  $T_{g(L)}$  and  $T_{g(U)}$ , due to the different techniques used to determine them, has established that a considerable variation can exist between one value and another depending of the method of analysis fundamentals and of the sample characteristics. This last condition has been the subject of several discrepancies in PALS results in polymers, since, due to the high sensitivity of this technique, almost any small variation in a polymer's sample conditions or characteristics, i.e., crystallinity, annealing, quenching, average molecular weight, etc., can modify widely the results and the reproduction of them for a same polymer becomes difficult.<sup>2</sup> In this study, the number-average molecular weight of PET samples is considered low in accord with the range of the average molecular weights of different commercial samples of PET reported, which ranges from 15,000, for certain films and textile fibers, to 45,000, for blow-molded soft-drink bottles. This, obviously, has to influence the obtained results, with both glass transition temperatures appearing at lower regimes than those expected.

The double glass transition behavior noticed in the analyzed polymers is also characteristic of several other semicrystalline polymers.<sup>15</sup> The lower glass transition temperature,  $T_{g(L)}$ , is generally acknowledged to signify an increase in segmental mobility of the macromolecular chains within amorphous regions which are not constrained by the crystalline phase. The upper glass transition,  $T_{g(U)}$ , occurs at higher temperatures than  $T_{g(L)}$  and is

thought to be associated with an increase in segmental mobility resulting from the diminishing constraint imposed by the crystalline phase upon the surrounding glassy regions. The primary evidence supporting this theory is that increases in  $T_{g(U)}$  typically accompany increasing degrees of crystallinity.

The crystalline fraction ( $X$ ) was determined for nylon-6 and PET by DSC as was already mentioned, and the results were nylon-6 = 29.48% and PET = 20.15%. In accord with the double glass transition theory, since nylon-6 has a higher  $X$  than that of PET, the former polymer indeed presents a wider temperature range between  $T_{g(L)}$  and  $T_{g(U)}$ , approximately 20°C for nylon-6 and 15°C for PET (Figs. 2–5). Thus, due to that the crystalline domains are more extensive in nylon-6 than in PET, the required temperature, from  $T_{g(L)}$ , to break the constraint imposed by the crystalline phase in nylon-6 and to reach its  $T_{g(U)}$  is higher compared with the same phenomenon in PET.

If the  $o$ -Ps lifetime does reflect the average size of free-volume cavities, the increases in slope for the lifetime–temperature plot (Figs. 2 and 4) are indicative of cavity growth as the temperature increases. Increased expansion of free-volume sites is consistent with the macroscopic increase in volumetric expansion which, as it is known, accompany glass transitions, thereby supporting this proposed interpretation of the lifetime response for both polymers. Using the following equation<sup>16</sup>:

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \left( \frac{1}{2\pi} \right) \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1}$$

where the intermolecular-space holes are assumed to be a spherical with a radius  $R$ ,  $R = (3V_H/4\pi)^{1/3}$ , and an electron layer of thickness  $\Delta R = 0.166$  nm, which is an empirical parameter determined by fitting the observed  $\tau_3$  with the known cavity sizes in molecular substrates; thus,  $R_0 = R + 0.166$ , where  $R_0$  is the radius of free-volume hole. The hole volume corresponding to  $\tau_3$  for the heating process was calculated and the results for nylon-6 and PET are shown in Figures 2 and 4, respectively, together with the lifetime. As can be observed in these figures, the mean size of free volume increases as the temperature increases.

At the initial temperature (30°C) and according with the free-volume size value, PET possesses a bigger mean size of free volume than does nylon-6. This can be influenced by the higher crystallinity in nylon-6 with respect to PET, as determined by

DSC, since a larger free volume is expected to be found in the amorphous region and in this zone, mainly, is where changes in the molecular mobility occur during  $T_g$ .

Further information concerning to the glass transition behavior can be obtained from the response of  $I_3$  to temperature. Considering the hypothesis that free volume is isolated at chain ends at a temperature close to the glass transition,<sup>17</sup> the density of free-volume cavities would be expected to be relatively constant in this temperature regime. Assuming that the slope of the intensity curves is dependent upon the number of free-volume sites being generated as the temperature is changed, the slope would be small near  $T_{g(L)}$ . This situation, effectively, occurs in both studied polymers, as can be observed in Figures 3 and 5. Considering nylon-6,  $I_3$  tends, in general, to diminish as the temperature increases (Fig. 3). This behavior can be explained by the spur model for positronium formation, since it is possible to assume that positrons are trapped in a higher proportion when nylon-6 chains become more elastic.<sup>18</sup> It is well known that polyamides have hydrogen bonds between amide groups, which confer their characteristic structure and properties; thus, at room temperature, these polymers are glassy, and under this condition, the positrons feel just a moderate dipolar field, but when the temperature rises (above  $T_g$ ), the polyamides become rubbery and this promotes a more disordered state in their structures, and in this electronic environment, the positrons can be trapped more efficiently by the strong dipole occurring in the amide groups, provoking a diminution in  $o$ -Ps formation. A similar inhibition of Ps formation has been suggested recently for the carbonyl groups formed by thermal oxidation in polyethylene.<sup>19</sup> Another interesting situation for nylon-6 rises from the fact that  $I_3$  is larger at the minimum temperature of the analyzed range (below  $T_g$ ). This phenomenon can be understood by appraising the Ps formation models and the changes occurring in the polymer microstructure with a thermal treatment, which are described as follows:

- (a) Below  $T_g$ , polymeric chain local movements are reduced gradually; the microvoids that are blocked by local movements when the polymer is in a rubbery state are now available, at this temperature regime, as Ps localization sites. As a consequence,  $I_3$  increases below  $T_g$ .
- (b) Electronic density remains more homogeneous as a consequence of a “freezing” in

the movements of atoms in the polymeric chains; therefore, in accord with the spur model, the yield of Ps increases.

- (c) During the irradiation of the polymer with positrons, free electrons are produced by ionizing processes. Below  $T_g$ , these electrons could be trapped by positrons before they can recombine between them. Thus, the probability of a positron to get a free electron and to form Ps is augmented.

A distinct behavior in  $I_3$  was obtained for PET. In Figure 5 it can be observed that  $I_3$  augments as does the temperature, being more evident after  $T_{g(U)}$ . Therefore, it seems that the increase in the intensity of formation of *o*-Ps, in the vicinity of  $T_{g(L)}$ , can be attributed to the augmentation in the segmental mobility of PET chains, which provokes growing of new free-volume sites. Above  $T_g$ , the polymeric chains in the amorphous region are more flexible and more mobile; thus, as a consequence of the enlargement of the amorphous region,  $I_3$  continues increasing. In addition, above  $T_{g(U)}$ , the increase of free-volume density has overcome the possible effect of positron and electron trapping by the ester dipole in PET, since the dipole in PET has not suffered an apparent drastic change in its electronic distribution during  $T_g$ , as in the case of the dipole present in nylon-6. In an early work,<sup>20</sup> it was considered that the discontinuities in  $I_3$  for PET are attributable to the structural relaxation emergence through a *trans-gauche* transition between ethylene groups and to the *cis-trans* configuration change between carboxyl groups in the PET chains.

From the free-volume size values calculated for PET, it is possible to approximate the free-volume fraction,  $f$ , since it has been considered<sup>21</sup> that the product of  $\tau_3 I_3$  or  $V_H I_3$  can be assigned to the measure of the fraction of intermolecular space. In addition, it is known that the free-volume fraction is related to  $T_g$  and the thermal expansion coefficient for that fraction,  $\alpha_f$ , by the following expression:

$$f = 0.025 + (T - T_g)\alpha_f$$

where it is assumed that the free-volume fraction at  $T_g$  is 0.025.<sup>22</sup> Then, if  $f$  can be obtained from *o*-Ps parameters,  $\alpha_f$  can be calculated using the prior equation. Thus, at 50°C [onset of  $T_{g(U)}$ ],  $f (=V_H I_3)$  is 0.015; using this value to calculate  $\alpha_f$  at approximately  $T_{g(U)}$  and at a lower temperature, the results are as follows:  $\alpha_f(\sim T_g) = 9E^{-3}$  and  $\alpha_f(<T_g) = 1.9E^{-3}$ . The onset of  $T_{g(U)}$  is considered at 50°C, in accord with the slope change observed in Figures

4 and 5 at that temperature. As expected, the thermal expansion coefficient at a quasi-glassy state [45°C, between  $T_{g(L)}$  and  $T_{g(U)}$ ] is lower than that obtained for the rubbery state of PET. Also, this is in agreement with the increase of the free-volume fraction in PET as the temperature is increased. Similar determinations of thermal expansion coefficients utilizing Ps parameters have been carried out in epoxy resins.<sup>14</sup> Since  $I_3$  is considered to be affected by the changes in electron density in the chemical structure of nylon-6, during its thermal treatment, an analysis alike to that for PET is inappropriate.

Regarding  $T_c$  detected in nylon-6, this has already been observed by DSC<sup>23</sup> at a temperature of 70°C. It is known that  $T_c$ , for any polymer that possesses it, does not occur at a specific temperature, since it has a large dependence on polymer morphology, i.e.,  $T_c$  increases as the longitude of folded chains in a polymer does.

## CONCLUSIONS

The analysis of the lifetime and intensity of formation of the *ortho*-positronium results has afforded interesting insight both into the effects of heat treatment on the density and mean size of the free volume and into the dependence of glass transition processes on free-volume characteristics.

Glass transition behavior was evident in the lifetime behavior of both polymers studied. Augments in slope of the lifetime-temperature plots were interpreted to suggest that glass transitions are followed by increased free-volume cavity expansion as temperature is increased, which was demonstrated by the free-volume mean size values calculated. The *o*-Ps intensity of formation responses in the vicinity of the upper glass transition agreed with the association of this transition with the reduction of crystalline constraint on segmental mobility in the amorphous phase, especially for PET. The intensity behavior in nylon-6 is in better accord with distortions occurring in the electronic density surrounding the amide groups due to the glass transitions.

Using PALS, it was possible to detect two glass transition temperatures for two semicrystalline polymers, which had not been previously observed and which is difficult by applying other techniques. Since the glass transition temperatures and other relaxations in polymers have a great importance by their relation to viscoelastic properties, the application of a virtually novel technique to detect them, with a molecular level sensitivity and with the pos-

sibility to calculate free-volume parameters, offers a good alternative.

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