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Positron Annihilation Studies of the Glass–Rubber Transition in Poly(alkyl methacrylates)

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ABSTRACT: Positron annihilation lifetime measurements are reported on poly(methyl methacrylate), poly(ethyl methacrylate), poly(isobutyl methacrylate), and poly(*n*-butyl methacrylate) over a temperature range that includes the glass transition temperature. The long-lifetime component exhibits a similar variation to that observed in similar glass-forming simple liquid systems. The interpretation of the data based on a free-volume model and using ultrasonic data to define a mean cavity size allowed rationalization of the data on all the systems. A close inspection of the variation of the intensity of the long-lifetime component, τ_3, showed evidence for the effects of motions associated with the alkyl side chains on the free-volume in the solid polymer and hence on the probability of formation of orthopositronium.

Introduction

Technologically the glass–rubber transition (T_g) is perhaps one of the most important characteristics of an amorphous polymer. During the last 30 years a number of theories have been put forward to explain this phenomenon and all involve the concept of entropy or free volume as being the controlling feature associated with the T_g process.[1] Studies of the specific heat,[2] modulus of elasticity,[3] coefficient of self-diffusion,[4] and mechanical,[5] dielectric,[6] and ultrasonic[7] relaxation have all been interpreted on the basis of the free-volume model. The free-volume model[8] has been widely applied to the interpretation of the physical properties of glassy polymers. Our previous studies of glass-forming liquids[9–11] have indicated that the positron annihilation technique is capable of probing the temperature variation of the cavity size in which it is formed. The latter appears to be closely related to the free volume, which is used to describe the temperature dependence of the glass transition processes as observed by many relaxation techniques. The position annihilation technique has been used extensively for the investigation of the glass–rubber transition in polymer systems,[12–36] and this topic has been recently reviewed by Stevens.[36] In this paper we attempt to explore the use of positron annihilation for the characterization of the glass–rubber transition in a system in which both backbone and side chain motion is also possible.

Many studies have been reported on positron annihilation in polymers; however, many of these studies use commercial polymers of ill-defined composition, thermal history, or molecular weight. Despite these limitations on the definition of the system, it is clear that the method is capable or providing useful information on the glass state of polymers. The positron on entering the solid will induce ionization of the material through which it passes, generating free electrons and losing energy in the process.[37] Positronium is formed and trapped into a cavity.[38] If the spins of the positron and electron are antiparallel, parapositronium is formed, whereas if they are parallel orthopositronium is formed. The annihilation of parapositronium is quantum mechanically allowed and occurs in 125 ps, whereas annihilation of orthopositronium would take approximately 140 ns in a vacuum.[39] Annihilation of the orthopositronium occurs via pick-off[12] processes, the probability of which is directly related to the inverse of the cavity dimensions and to the electron density of the cavity wall. The lifetime of the orthopositronium is therefore directly related to cavity size,[9] which in turn reflects the free-volume distribution in the polymer solids.

Positron annihilation lifetimes have been measured as a function of temperature,[12,20] pressure,[36], and electric field[2,3,25,30] in nylon, polyethylene, elvicite, polystyrene, poly(vinyl chloride), Teflon, and polyisoprene.[12,20,23–25,30,36] The majority of the samples used were commercial in origin and probably contained plasticizer and antioxidant as well as fillers. There have, however, been a number of studies in which the polymers were better characterized and these reveal the strength of the technique to provide data on the free-volume distribution in the system. Studies by Stevens et al.[20,21] on two well-defined polymers, poly-

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Table I
Characteristics of Polymers

polymer	$M_n \times 10^3$	M_w/M_n	density, kg/m^3	T_g, K	tacticity[a]
poly(methyl methacrylate) (PMMA)	145	3.59	1200	376	60% s, 36% h, 4% i
poly(ethyl methacrylate) (PEMA)	110	2.72	1110	340	
poly(isobutyl methacrylate) (PIBMA)	101	2.78	1090	324	48% s, 52% h, 0% i
poly(*n*-butyl methacrylate) (PNBMA)	71.3	2.49	1070	293	

[a] s = syndiotactic, h = heterotactic, i = isotactic.

Table II
Average Values of Free Positron Lifetime (τ_2), Orthopositronium Lifetime (τ_3), Parapositronium Intensity (I_1), Free Positron Intensity (I_2), and Orthopositronium Intensity (I_3) at Temperature T (K)[a]

material	T, K	$\tau_2 \pm \Delta\tau_2$, ns	$\tau_3 \pm \Delta\tau_3$, ns	$I_1 \pm \Delta I_1$, %	$I_2 \pm \Delta I_2$, %	$I_3 \pm \Delta I_3$, %
PMMA	304	0.383 ± 0.012	1.96 ± 0.02	22.3 ± 1.8	45.4 ± 1.5	32.1 ± 0.5
PEMA	299.9	0.389 ± 0.009	2.2 ± 0.02	15.9 ± 1.8	51.0 ± 1.6	32.9 ± 0.3
PNRMA	301.5	0.367 ± 0.007	2.16 ± 0.02	19.9 ± 1.5	55.1 ± 1.4	24.9 ± 0.3
PIBMA	299.1	0.381 ± 0.009	2.23 ± 0.02	12.6 ± 1.5	53.4 ± 1.4	33.9 ± 0.4

[a] The parapositronium lifetime has been fixed at 0.125 ns. $\Delta\tau_2$, $\Delta\tau_3$, ΔI_1, ΔI_2, and ΔI_3 are the errors in τ_2, τ_3, I_1, I_2, and I_3, respectively.

styrene and polyisobutylene, have been interpreted in terms of free-volume models and also the possibility of segmental contributions to the annihilation process. In our previous studies of glass-forming liquids we were able to identify the following transitions: a low-temperature change in the long-lived lifetime, τ_3, associated with the generation of free volume, the T_g phenomenon, and a higher temperature characteristic associated with the lifetime of the orthopositronium, being comparable with the relaxation of the material forming the cavity wall.[9-11] In the poly(alkyl methacrylates) we may anticipate observing the effects of backbone relaxation and also the influence of the motion of the side chains on the total dynamic spectrum.[7] Using the concepts validated for simple glass-forming liquids, we will also attempt to explore further the nature of the annihilation process in polymers and correlate the observed behavior with the relaxation[40] properties of the matrix as sensed by techniques such as ultrasonics[41] and dielectric relaxation.[42]

Experimental Section

Materials. The polymers used in this study were obtained from du Pont de Nemours and were reprecipitated before being used. The samples of the polymer were pressed into disks of thickness 2 mm by compression molding for 12 h T_g + 40 K under a pressure of 14 MN/m^2. Glass transition temperatures, Table I, were determined with a Perkin-Elmer DSC-1 at a heating rate of 8 K/min. Densities were measured to ± 0.2% by a liquid immersion method. Polymer tacticities were determined from the relative intensities of the methane resonances using 100-MHz ^{1}H NMR spectroscopy at room temperature in CDCl$_3$ as solvent. The structures conform closely to those reported in the literature.[43] Molecular weights were determined by gel permeation chromatography. The molecular weight distributions were uncorrected for the finite resolving power of the columns and so are likely to be rather narrower than quoted.

Positron Annihilation Measurements. Lifetime spectra were obtained with a conventional fast–slow coincidence system. The positron source used in this study was ^{22}NaCl evaporated onto and sealed between two Kapton foils. The details of the experimental system used in these studies have been described elsewhere.[10] The samples of the polymers were molded into flat disks and then cut into square sections between which was placed the source. The samples were degassed and sealed into a Pyrex tube. The time resolution of the system was measured by observing the prompt curve of a ^{60}Co source and was found to be better than 400 ps. The source correction (6%) was determined by measuring the positron annihilation lifetimes of benzophenone crystals. Each spectrum contained nearly 5 × 10^5 events and was analyzed by using the computer program POSITRONFIT EXTENDED, developed by Kirkegaard et al.[44] The measurements were carried out as a function of temperature, the thermostating being better than ±0.1 K over the whole range.

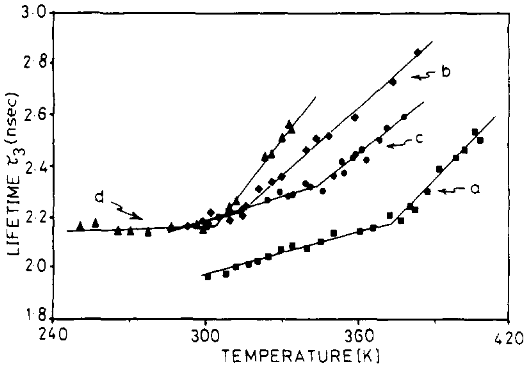

Figure 1. Variation of orthopositronium lifetime, τ_3, as a function of temperature for PMMA (curve a), PIBMA (curve b), PEMA (curve c), and PNBMA (curve d).

Each lifetime spectrum could be resolved into three components. The variance of the fit was improved by constraining one of the components to have a lifetime of 125 ps the para component. Average values of the lifetimes for the polymers studied are listed in Table II, for the glassy and rubbery phases. It was clear that the shortest and intermediate components do not show any significant variation with respect to structure of polymer, temperature, or phase. However, both the lifetime and the intensity of the longest-lived component are sensitive to the structure and form of the polymer.

Results and Discussion

Intensities and Lifetimes for Poly(alkyl methacrylates). The lifetime spectra were all resolvable into three components: τ_1, τ_2, and τ_3 with corresponding intensities I_1, I_2, and I_3. The two shortest components, τ_1 and τ_2, are attributed to the annihilation of the parapositronium and free positrons, respectively. The observation that τ_2 does not vary significantly over the temperature range used in these studies implies that the average electron density does not change significantly. The longest-lived component τ_3, Figure 1, does, however, exhibit a marked temperature dependence and resembles that previously reported for the specific volume variation.[45] The lifetime τ_3, attributed to the decay of orthopositronium, increases slowly up to the glass transition T_g, after which it shows a continuous increase with steeper slope. The glass transition temperature predicted from the present

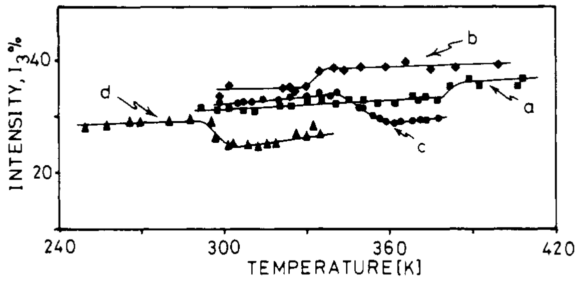

Figure 2. Variation of orthopositronium intensity, I_3, as a function of temperature for PMMA (curve a), PIBMA (curve b), PEMA (curve c), and PNBMA (curve d).

measurements is slightly lower than those determined by using pseudoequilibrium observations.[8] This has been observed with other systems and is usually attributed to the fact that thermalization of the positronium leads to a rise of the local energy of the cavity, hence allowing the onset of creation of free volume to be detected at a slightly lower temperature than monitored by other techniques.[9]

The variation of the intensity I_3, corresponding to the longest lifetime component τ_3, is presented in Figure 2. Theoretically the ratio of the parapositronium to orthopositronium intensities should be 1:3. Deviations from this theoretical value have been observed in molecular liquids and crystals. Recently, attempts have been made to explain this deviation on the basis of the effects of molecular electron processes on the probability of orthopositronium formation.[47] No clear understanding of these phenomena appears to exist at the present time. It is observed in the case of the poly(alkyl methacrylates) that I_3 increases slowly with increasing temperature up to T_g, after which a sudden increase of approximately 5% is observed for PMMA and PIBMA whereas for PEMA and PNBMA a decrease of similar magnitude is observed.

Mechanism of Positronium Annihilation. A number of models have been proposed for the annihilation of positrons in the condensed phase. Formation of the positronium and its trapping into a cavity can be explained by using the concepts of the spur model. The probability of trapping positronium into a cavity will depend upon the range of the free delocalized state compared with the frequency and size of the cavities in that volume and also the Ore gap energy relative to kT. We will discuss this quantitatively later in the paper. The lifetime of the orthopositronium depends on the pick-off rate, which, according to Brandt,[12] reflects the overlap of the positronium wave function with that of the molecules forming the cavity. Hence the larger the cavity, the smaller the overlap and thence the longer the lifetime. The analysis of the cavity distribution in the glassy state has been discussed, recently with reference to supercooled *o*-terphenyl and phenyl ether.[9,10] We will follow the same general method of analysis in this paper.

Analysis of the Orthopositronium Lifetime Data. In the case of the simple glass-forming liquids studied previously we found that the shape of the lifetime τ_3, curve above T_g could be represented by a modified free-volume model. A striking difference between the behavior observed in the case of the poly(alkyl methacrylates) and the simple liquid glasses is that the onset of molecular motion in the lattice does not produce the comparable change in the temperature dependence of τ_3 observed in the latter systems.

Qualitatively the lifetimes τ_3 at T_g are similar; however, their absolute values do change with the nature of the structure of the polymer backbone. The values of the lifetimes τ_3 below T_g are also not identical, reflecting once again the differences in the structure. It is relatively easy to visualize that in PNBMA and PEMA quite extensive motion of the alkyl side chains will occur below T_g. As a consequence, larger cavities will be generated by the restricted motion of the side chains; this will influence the orthopositronium lifetime data. Qualitatively this increased degree of molecular mobility in PNBMA, PEMA, and to a lesser extent PIBMA is reflected in higher values of τ_3 below T_g. Above T_g the polymers all show markedly different temperature dependences of the orthopositronium lifetime τ_3 with temperature.

In simple glasses the o-Ps lifetime, τ_3, region just above T_g has been adequately described in terms of an extension of the Cohen and Turnbull theory.[47] The free volume in the sample is assumed to have the form

$$a = a_0 e^{-\gamma v_c/v_f} \tag{1}$$

where a_0 is the free-volume radius of the cavity, γ is the overlap factor, which has a value between 0.5 and 1, depending upon the geometry of packing in the liquid, v_c is the critical volume for positronium formation, and v_f is the volume of the bubble containing the positronium. Rusch[48] has discussed this distribution function in terms of the probability $P(t)$ of segmental rearrangement and shown that the relaxation time t_p at a temperature T_1 can be related to its comparable value at another temperature T_2 by a shift factor a_T. This factor has the form

$$a_T = t_p(T_1)/t_p(T_2) \tag{2}$$

where T_2 is chosen to be a reference temperature. Williams et al.[49] have obtained an empirical relationship correlating the shift factor, a_T, with the glass transition temperature—the WLF theory. Hence it can be seen that the WLF theory is intimately connected with the distribution of free volume in the systen and hence to the temperature dependence of the o-Ps lifetimes. The shift factors for the polymers investigated in this paper have been determined by using dielectric relaxation. We have shown previously that rationalization of the lifetime data is only possible if the temperature dependence of a_0 is obtained and that this is best obtained from ultrasonic propagation data.[9,10] With these data it is possible to compute the function ln $(\lambda_T a_T/a_0)$, where λ_T is the o-Ps pick-off rate at a given temperature, and when these data are plotted against the density for different polymers, linear relationships are observed over the entire temperature range for a given polymer. This implies that the same model developed for the simple glasses can be applied in the case of these polymers. Further the observed slight deviations from linearity in the region of the T_g are a direct consequence of the differences in the effective time scales of observation of o-Ps and ultrasonics. Strictly speaking, the time scales of these observations should be identical; however, in practice the o-Ps senses the cavity distribution on a time scale of 10^{-9} s whereas the corresponding ultrasonic experiment is performed at 10^{-7} s. The slight differences are reflected in the deviation of the data from the ideal linear relationship and are most pronounced in the region of T_g.

The variation of the annihilation rate λ_3 with temperature can be expressed by the relationship

$$\lambda_3 = B a_0 a_T^{-1} e^{\alpha\rho} \tag{3}$$

$$= B a_0 e^{-v_c/v_f} e^{\alpha\rho} \tag{4}$$

where a_0 and B are constants characteristic of a given polymer. Using eq 4, we will now consider the nature of the glass transition process.

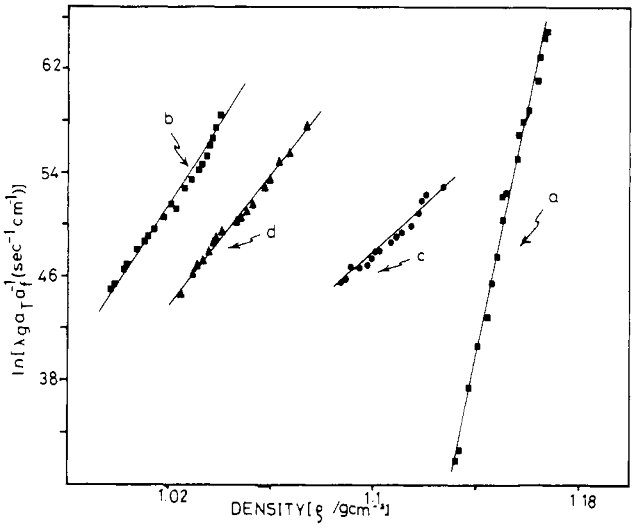

Figure 3. Variation of ln $(\lambda_3 a_T a_f^{-1})$ (where λ_3 is the orthopositronium annihilation rate (see^{-1}), a_T is the shift factor, and a_f is the free-volume radius (cm)) as a function of density, ρ (g cm^{-3}), for PMMA (curve a), PIBMA (curve b), PEMA (curve c), and PNBMA (curve d).

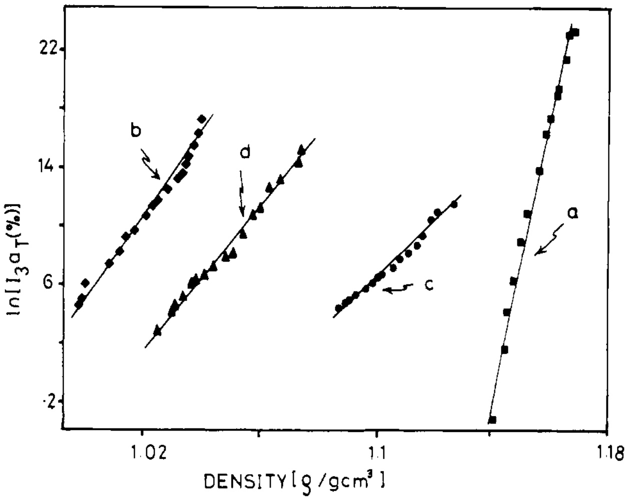

Figure 4. Variation of ln $(I_3 a_T)$ (where I_3 is the orthopositronium intensity (%) and a_T is the shift factor) as a function of density, ρ (g cm^{-3}), for PMMA (curve a), PIBMA (curve b), PEMA (curve c), and PNBMA (curve d).

Variation of I_3 with Temperature. Plotting the function ln $(a_T I_3)$ against temperature indicates significant differences in the variation of the function for the various studies, Figure 4.

It has been reported[50] recently that the probability of o-Ps formation reflected in its intensity can be expressed as

$$I_3 = \tfrac{3}{4}\phi_0 e^{-\gamma v_c/v_f} \tag{5}$$

where γ is placed equal to unity and ϕ_0 is the Ore gap formation probability. Assuming that I_3 has the form

$$I_3 = A e^{\alpha\rho} e^{-v_c/v_f} \tag{6}$$

where A and α are constants characteristic of the polymers, combining eq 5 and 6 yields

$$\phi_0 = \tfrac{4}{3} A e^{\alpha\rho} \tag{7}$$

which indicates the explicit dependence of the probability of formation of the o-Ps on the density of the material. This had been indicated earlier in the literature in a qualitative manner.[50]

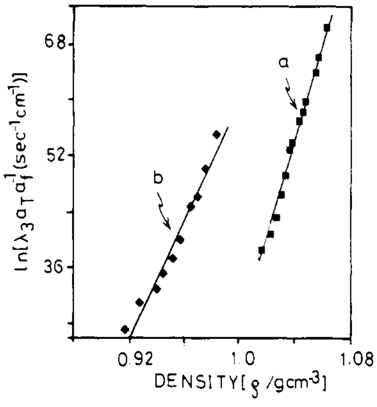

Figure 5. Variation of ln $(\lambda_3 a_T a_f^{-1})$ (where λ_3 is the orthopositronium annihilation rate (s^{-1}), a_T is the shift factor, and a_f is the free-volume radius (cm)) as a function of density, ρ (g cm^{-3}), for polystyrene (curve a) and polyisobutylene (curve b).

Inspection of the data in Figure 1 indicates that the values of I_3 below T_g reflect the densities of the polymer, being highest in PMMA and lowest in PNBMA. The correlation illustrates the premise that the probability is related to the density and hence the value of the Ore gap. In a polymer a further complication is the ability of the molecule to exhibit various types and combinations of molecular motion. In PMMA and also PIBMA the only motions available are rotation of the methyl top attached to the backbone and the rotation of the ester and ether linkages. The isobutyl group on the side-chain ester is relatively hindered and its motion is intimately connected with that of the ester. In contrast, in PEMA and PNBMA there is the possibility of additional motion of the alkyl side chain. The intensity of the o-Ps will also reflect the fraction of the total free volume available for the formation of the cavity. In the former polymers the motions released at T_g involve relatively cooperative motions of large elements of the backbone, in contrast to the latter, where side chains are executing facile motions below T_g. As a consequence the volumes of the cavities above T_g are influenced by the motion of the side chains and an apparent decrease in the intensity is observed. This latter effect is a consequence of the side-chain motions of the alkyl entities being comparable with the lifetime of the orthopositronium and is analogous to the higher temperature change observed in the lifetime data in simple liquid-forming glasses.

Correlations for Other Polymers. In an attempt to establish whether the approach outlined above for the analysis of the positronium annihilation data is completely general, we have analyzed data reported in the literature for polystyrene[20] and polyisobutylene.[21] These polymers are assumed to be amorphous and free from fillers or other impurities. It can be seen from Figures 5 and 6 that this analysis also holds for these polymers, which are very different both in structure and in their magnitude of T_g from those studied here.

Conclusions

The study described above illustrates the way in which the structure of the poly(alkyl methacrylates) influences the positronium annihilation. As in the case of simple glass-forming liquids, the variation of the orthopositronium lifetime, τ_3, above T_g can be correlated with a free-volume distribution model in which the mean cavity radius is defined by using a dynamic method—ultrasonic velocity. The data further illustrate the way in which the motion of the side chains in the polymer influences the overall

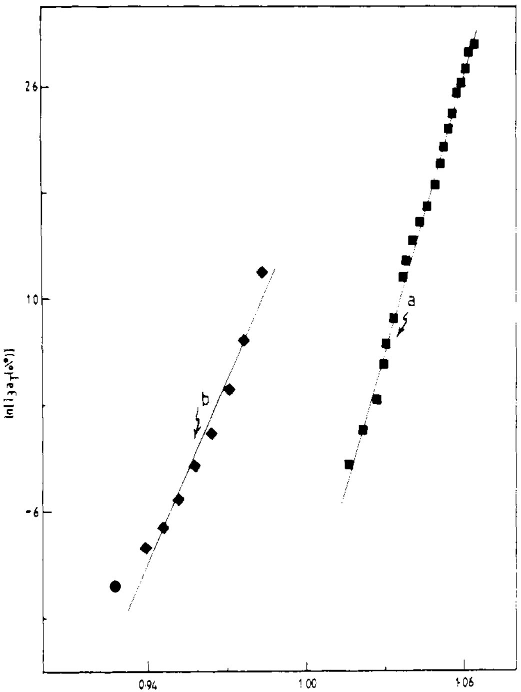

Figure 6. Variation of ln (I_3a_T) (where I_3 is the orthopositronium intensity (%) and a_T is the shift factor) as a function density, ρ (g cm^{-3}), for polystyrene (curve a) and polyisobutylene (curve b).

annihilation behavior of orthopositronium atoms.

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Registry No. PMMA, 9011-14-7; PEMA, 9003-42-3; PIBMA, 9011-15-8; PNBMA, 9003-63-8.

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