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Temperature and time dependence of orthopositronium formation in polystyrene

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Abstract

Three measurement protocols were performed to investigate the temperature dependence of positron lifetime spectra for polystyrene over the temperature range -70 to 180°C. The polystyrene samples were first subjected to a heating schedule in sequential 10°C increments. This was followed by a cooling schedule, again in 10°C increments. The third schedule involved rejuvenation of the specimen above T_g between each measurement. The measured lifetime spectra were resolved into three components. We observed a minimum in the temperature dependence of the o-Ps intensity I_3 at $\sim$20°C for polystyrene specimens subjected to the heating and cooling schedules, but not for the rejuvenated samples. The influence of the duration of e^+-irradiation on the lifetime and intensity of o-Ps annihilation was investigated under isothermal conditions. A decrease in o-Ps intensity I_3 with duration of exposure to e^+-irradiation was found whose rate was maximal at 23°C. The results suggest that the time dependence of the o-Ps intensity in the glass can be interpreted within the framework of the spur-model. Specifically, the variation of I_3 is ascribed to the formation at low temperature of free radicals with small electron affinities. After correcting for the e^+-irradiation effect, no significant aging effect in the glassy state was detected in the o-Ps intensity and lifetime. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Positronium formation probability; Radiation effects; Aging effect

1. Introduction

During the last several years many positron annihilation lifetime (PAL) measurements have been carried out with the aim of characterizing free volume in a wide variety of polymeric materials [1–3]. It has been demonstrated that the PAL technique is uniquely sensitive to free volume-based structural changes (glass transitions, relaxation processes) in polymers. The basic idea underlying this approach to relaxation phenomena is that molecular mobility at any temperature depends on the available free volume at this temperature.

The positron lifetime spectra of polymers can usually be described in terms of three exponential components. The term with the shortest lifetime (0.1–0.3 ns) is usually associated with annihilation of p-Ps and free positrons, the intermediate lifetime (0.3–0.5 ns) with positrons and positron-molecular species, and the longest lifetime (1–3 ns) with the decay of o-Ps by electron pick-off. The annihilation of o-Ps in polymers is essentially controlled by the free volume characteristics of the polymer. Once formed, o-Ps diffuses through the material and tends to localize in regions of reduced 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 localization sites. A semiempirical correlation between the free volume hole radius R and the o-Ps lifetime τ_3 has been established [4,5],

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

where the boundary layer thickness $\Delta R = 0.1656$ nm has been determined empirically by fitting Eq. (1) to o-Ps annihilation data for molecular solids of known pore sizes. Besides the o-Ps lifetime τ_3, the corresponding intensity I_3 of the o-Ps pick-off component is indicative of both the Ps formation probability and the density of localized sites.

Despite numerous studies of positron annihilation in polymers, much controversy exists regarding the theoretical basis for interpreting positron annihilation spectra, and the application of analytical methodology for extracting free

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volume parameters from experimental data. Several effects contribute to this situation. First, the interaction of high-energy positrons with a polymeric material during the thermalisation which follows their injection, is a complex process involving phenomena such as ionization, electron–ion recombination, free radical formation as well as trapping of e^- and e^+. This leads to uncertainty not only in the quantum mechanical basis for relating o-Ps lifetimes to free volume cavity sizes, but also to difficulties of interpreting anomalous effects of e^+-irradiation which are the principal focus of this paper. Second, the level of free volume in polymeric materials is often dependent on the processing or formation history, and, in the glassy state, may be time-dependent (physical aging [6–11]). This results in difficulties in comparing data on polymers generated in different laboratories. Recently, studies of the influence of e^+-irradiation time on the positron lifetime spectra of polymers have been carried out. It was observed that [12,13] the o-Ps intensity decreased with increasing elapsed time after insertion of the source. The extent to which the o-Ps intensity decreases with e^+-irradiation time was found to depend on the type of polymer, the positron flux and the temperature. Thus, variations in the extent of e^+-irradiation could be another source of disagreement between PALS results from different laboratories.

In this paper, positron lifetime spectra were measured on well-characterized polystyrene samples as a function of temperature and e^+-irradiation time. By investigating the effect of different thermal histories on o-Ps annihilation lifetimes and intensities, it is hoped to develop greater understanding of the factors which influence positronium formation probability in polymers.

2. Experimental

2.1. Sample preparation

Pure polystyrene (PS) with a molecular weight of 153 000 was used in this study. The materials were supplied in pellet form. These specimens having a thickness of 1 mm were formed under 7.5 ton pressure and annealed at 170°C for 48 h, after which they were cooled down to room temperature.

2.2. Positron annihilation lifetime spectroscopy

The lifetime spectra were recorded with a fast–fast lifetime system having a time resolution of 220 ps. Each spectrum contained 1×10^6 counts accumulated over a period of about 0.5 h. The positron source was rather strong (50 μCi ^{22}NaCl, placed between two 1.7 mg/cm^2 aluminum foils) for the purpose of shortening the measuring time. The source and the sample were then placed in a thin-walled aluminum vacuum chamber for the duration of the experiments. Heating wires mounted at two opposite sites of the sample holder and two diode temperature sensors mounted inside the sample holder were connected to a temperature controller (Model 330, Lake Shore Cryogenics). A constant temperature was maintained to within ± 0.05°C during data acquisition periods.

Three measurement series were performed on the temperature dependence of positron lifetime spectra. Each series differed in the treatment of the samples in the temperature interval from -70 to 110°C. Prior to measurement, the samples were annealed at 95°C (slightly above T_g) for 30 min and quickly cooled down to -70°C at a rate of 10°C/min. Then the temperature was raised from -70 to 110°C in steps of 10°C. At each measurement temperature the samples were thermally stabilized for 40 min before initiating the collection of a lifetime spectrum. Next, the specimen was again cooled from 110 to -70°C in steps of 10°C and lifetime spectra were obtained at each temperature. Finally, the samples were annealed in the chamber at 95°C and cooled at a rate of approximately 10°C/min to the measured temperature. Spectra were recorded at increments of 10°C in the temperature range from -70 to 180°C. After each measurement below 95°C, the samples were rejuvenated for 30 min at 95°C, in the rubbery state. This rejuvenation procedure [14,15], was used in our earlier o-Ps studies of polymers in the glassy state, and is designed to minimize anomalous decreases in o-Ps intensity resulting from prolonged exposure to e^+-radiation. Finally, the temperature was increased stepwise from 100 to 180°C and measurements taken at 10°C increments. The influence of e^+-irradiation exposure on the positron annihilation spectrum was investigated using a polystyrene sample which was annealed at 95°C in vacuum for 6 h and then cooled slowly to room temperature (23°C). The sample was then stored at room temperature for 20 days in order to produce a well-aged specimen. The time dependence of o-Ps intensity was first evaluated at 23°C immediately after source installation. For measurements at other temperatures, the samples was annealed in the chamber at 95°C for about 6 h, then cooled to the measurement temperature at a rate of 10°C/min, and the measurement began immediately after 40 min thermal equilibration.

3. Results and discussion

The measured lifetime spectra were all resolvable into three components using the PATFIT computer program [16], and the variances of the fits (χ^2) are smaller than 1.2. Of the three components, only the o-Ps pick-off lifetime τ_3 and intensity I_3 showed systematic variations with temperature. Fig. 1a shows the temperature dependence of the o-Ps lifetime τ_3 for the same polystyrene sample but with three different thermal treatments. Within the scatter of the data we detect no differences in τ_3. This indicates the o-Ps lifetime does not depend on the thermal history of the materials. Taking τ_3 as a measure of the relative free volume cavity size (according to Eq. (1)), the deviation of the

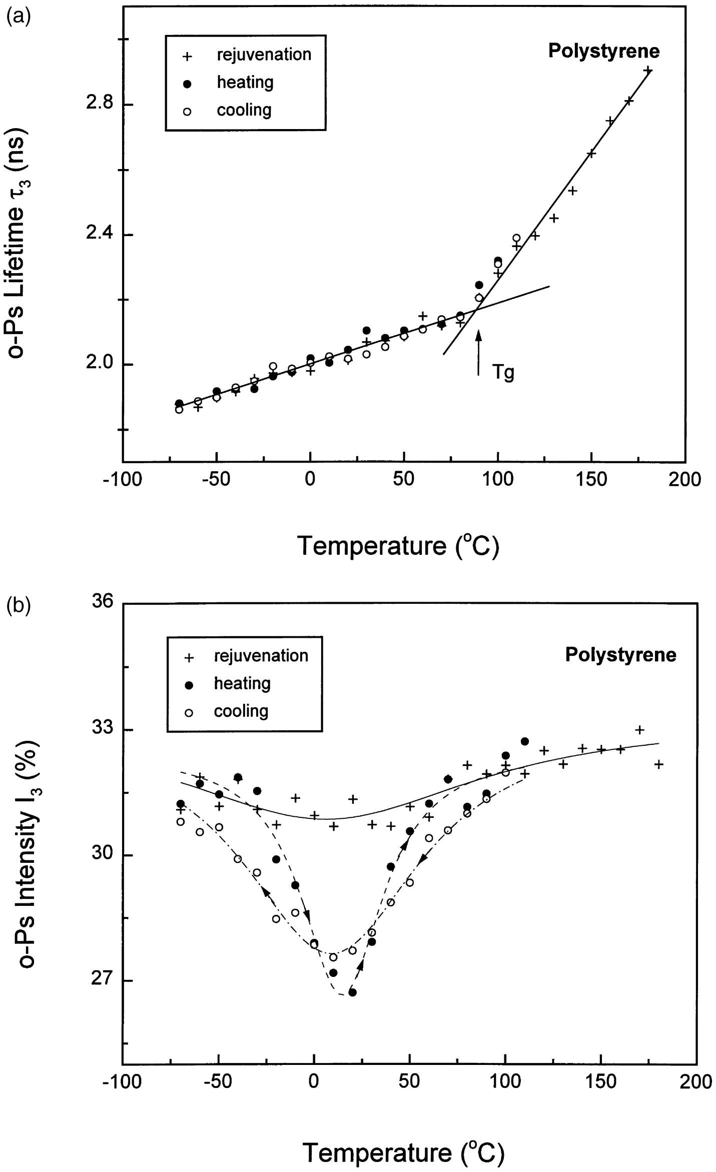


Fig. 1. The temperature dependence of (a) o-Ps lifetime τ_3 and (b) the corresponding intensity I_3 for polystyrene samples with different thermal treatment.

thermal response noted in each polystyrene sample at 87.3°C indicates a sudden increase in thermal expansion coefficient of the free volume cavities, which is consistent with the occurrence of a glass transition. Such behaviour of τ_3 has been observed for many different polymers. Interestingly, the glass transition temperature measured from τ_3 is lower than the bulk value measured by d.s.c. (T_g = 107.6°C). This has been reported for other polymers, and is often attributed to the fact that the duration of measurement by PAL at each temperature is much longer than that by d.s.c., leading to relaxation of the free volume near T_g.

The corresponding variation of the o-Ps intensity I_3 is presented in Fig. 1b. While no significant differences in τ_3 were measured for the samples with different thermal treatments, different values of I_3 were obtained in the glass when comparing rejuvenated samples versus samples subjected to sequential heating/cooling schedules. For the latter, I_3 exhibits a distinct minimum value at a temperature near 20°C, while no such minimum is seen in the rejuvenated specimen. It is interesting that the I_3 minimum occurs at ca. 20°C, which is in the middle of the temperature range where the so-called β-transition of polystyrene is reported to occur (i.e. between ca. 10 and 50°C [17,18], depending on the molecular weight, tacticity and the specific measurement technique employed). The β-transition is believed to result from intramolecular relaxation associated with the phenyl groups [19–21], although there is still uncertainty about the precise nature of the transition. It should be mentioned that a similar albeit more dramatic minimum in I_3 has been previously reported in polyethylene and polypropylene [22–24]. Kindl and co-worker [22,23] suggested that the appearance of an I_3 minimum could be the superposition

Table 1
The comparison of o-Ps intensity, I_3, and o-Ps lifetime, τ_3, for the polystyrene at room temperature with different thermal history

	τ_3 (ns)	I_3 (%)
Well-aged	2.064 ± 0.020	31.11 ± 0.16
Heating	2.067 ± 0.025	26.71 ± 0.18
Cooling	2.045 ± 0.019	27.80 ± 0.15
Rejuvenating	2.059 ± 0.024	30.82 ± 0.18

of two effects: (1) a temperature-induced decrease of the number of voids suitable for Ps-atoms; and (2) freezing-in of local motions which opens up additional voids at low temperature. However, such an interpretation seems inconsistent with the fact that the I_3 minimum is not observed in glassy polystyrene samples subjected to rejuvenation. As shown in Fig. 1b, for the samples after rejuvenation, I_3 is essentially temperature independent over the whole temperature range. To further illustrate this, we give a comparison of I_3 and τ_3 values for polystyrenes with different thermal histories at room temperature in Table 1. The o-Ps lifetimes for all the samples are numerically very similar, but I_3 values differ substantially. Interestingly, I_3 for the rejuvenated samples is very close to the well-aged value at room temperature, while the thermally cycled samples were found to be significantly lower.

To interpret the o-Ps intensity we need to understand the mechanism of Ps formation. At present, the so-called spur model [25] appears to be the best description of Ps formation in condensed matter. Spur formation is reported to be dominant in polystyrene and several other polymers via depth profiling with positron beams [28]. When an energetic positron is injected into the polymer matrix, a trail of radiation damage is created, i.e. the positron spur, during which the kinetic energy of the positron is dissipated through creation of cations and free electrons. According to the spur model, Ps formation takes place in the positron terminal spur when electron–ion recombination, and scavenging and trapping of electrons and/or positrons are competing. The Ps formation process is therefore affected by several factors, including competition with electron-ion recombination, and formation of free radicals, which are sensitive to the chemical functional groups on the polymer structure. Generally, the free radicals have positive electron affinities, and may inhibit positronium formation by scavenging of excess electrons. The following competitive processes take place in the thermalized spur of injected positrons:

$$e^+ + e^- \rightarrow \mathrm{Ps} \quad \text{positronium formation}$$

$$M^+ + e^- \rightarrow M* \quad \text{geminate recombination}$$

$$e^- + \dot{R} \rightarrow \dot{R}^- \quad \text{electron capture by free radicals}$$

Once formed, Ps diffuses and tends to localize in cavities in the polymer matrix, such as free volume sites. The o-Ps intensity I_3 is therefore a function of the o-Ps formation probability, the numbers of e^- and e^+ trapping sites, and the number of free volume cavities. Thus, it is possible, a priori, that the I_3 minimum effect observed in the glassy state is due to e^+-irradiation effects or to changes in free volume due to physical aging.

Recently, however, it has been reported, for several polymers, that the intensity of the o-Ps lifetime component decreases with increasing elapsed time after insertion of the positron source [12,13]. These studies have clearly demonstrated that the effect is a consequence of the irradiation damage, and not to physical aging. In our experiment shown in Fig. 2, we see no decrease of I_3 with irradiation

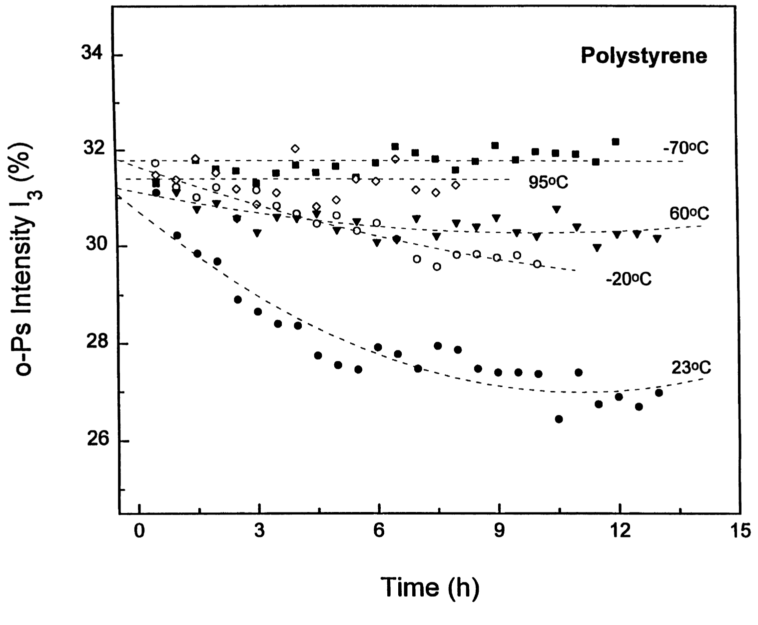


Fig. 2. The dependence on exposure time to the positron source of the o-Ps intensity, I_3, in polystyrene.

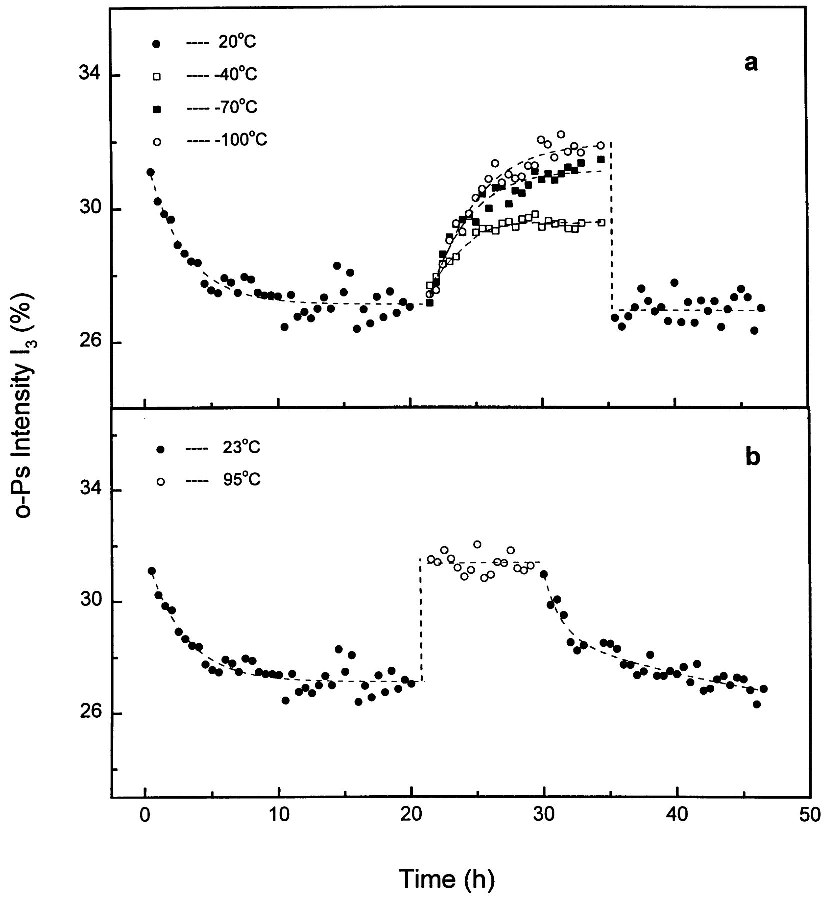
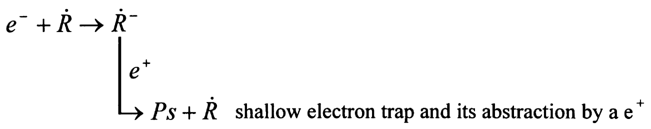


Fig. 3. The influence of the temperature on the e$^+$ exposure time dependence of the o-Ps intensity I_3 in polystyrene.

time at high (95°C) and low temperatures (−70°C). However, for intermediate temperatures, I_3 shows a substantial decrease with exposure time, although τ_3 remains unchanged. Since the sample had been stored at room temperature for 20 days, clearly, it seems unreasonable that physical aging is the origin of the effect, at least for the decrease of I_3 at room temperature. Also, consistent with this, in Fig. 1b, a similar I_3 minimum is observed in both heating and cooling series, despite the fact that the initial heating treatment will erase the prior thermal history of the sample. Thus, the observed I_3 response must result from e$^+$-irradiation damage and not from a change in the free volume cavity concentration.

Fig. 3a,b shows the influence of different thermal histories on the e$^+$ exposure time dependence of the o-Ps intensity I_3 in polystyrene. As evident in Fig. 3a, after approximately 20 h of continuous source exposure at 23°C, the o-Ps intensity decreases from 31.4 to 27%. When next the temperature is suddenly decreased to −40, −70 and −100°C, I_3 increases slowly over a period of several hours and reaches a saturation value which is comparable to the initial value (31.4%). Subsequently, when the temperature is rapidly raised to 23°C, I_3 decreases immediately to a value which is essentially the same as that obtained after 20 h of positron irradiation at 23°C. In contrast, as shown in Fig. 3b, when the temperature is raised to 95°C, following 20 h irradiation at 23°C, I_3 increases sharply to a value comparable to the initial value, and stays at that level for 10 h irradiation duration. Subsequently, on cooling rapidly to 23°C, I_3 decreases slowly at a rate comparable to that during the initial irradiation step. We can only speculate at present on a possible explanation for these time-dependent phenomena. Previous authors [12,15] have interpreted the decrease in I_3 in the glass with e$^+$-irradiation time in the context of the spur model as due to the accumulation of species (ions and free radicals) that inhibit Ps formation through trapping the precursors (e$^+$ and/or e$^-$) of Ps. When the temperature is reduced through T_β to −70°C, the mobility of such species is progressively reduced. The present observation (Fig. 2), i.e. that the rate of accumulation of these species in polystyrene is maximal at temperatures near the β relaxation, is consistent with this picture. This follows if one assumes that the local motion which freezes in at the β relaxation temperature (e.g. phenyl group rotation), is necessary for ion–electron recombination reactions or the production of free radicals. However, to explain the time-dependent effects shown in Fig. 3a,b, a more detailed analysis is required. To interpret the slow increase in I_3 on cooling from 23 to −40, −70 and −100°C (Fig. 3a), it appears that we need to consider the accumulation of species which favour o-Ps formation at very low temperatures in the glass. In the context of the spur model, it appears that one possibility is, below the β relaxation temperature, T_β, trapped free radicals provide a source of electrons for the formation of o-Ps, resulting in an increase of I_3 with e$^+$-irradiation time. Both the increase of the o-Ps yield and the decrease of the inhibition efficiency of free radicals at low temperatures in polystyrene can be qualitatively understood by assuming that the e$^+$-radiation-induced radicals have small electron affinities and capture electrons to form a loosely bound complex [26,27]. Many reactions of excess electrons with free radicals result in the formation of a product in which the electron is comparatively weakly bound (i.e. by 1–2 eV). In such a case, the positron can efficiently react with the formed complex to produce Ps by picking off the electron. This process can be schematically described as:



shallow electron trap and its abstraction by a e$^+$

At very low temperatures, the free radicals produced in the positron spur are presumably immobilized and the decay rate constant decreases with storage temperature. With increase of irradiation time, the concentration of immobilized $\dot{R}^-$ will increase, and the weakly bound electron can probably tunnel from one $\dot{R}^-$ to another, becoming delocalized on several $\dot{R}^-$. This of course increases the electron mobility and the effective range of the electron wave function, and that, in turn, enhances further Ps formation at low temperature. With increase of temperature, when the sample is allowed to warm, these frozen radicals become labile and migrate, and the tunnelling effect becomes smaller. The electrons are trapped on the free radicals which results in a dramatic decrease of the mobility of the electron, and a reduction in range of the wave function compared to non-trapped electrons. The positron can still pick off electrons from $\dot{R}^-$, but the probability of this process is much smaller than that of Ps formation by a nontrapped electron. Hence we observe an inhibition of Ps formation with increasing temperature, below T_β. Moreover, on warming up the sample, reaction between free radicals and cations becomes possible, as well as ion–electron recombination, each of which decreases the probability of the loosely bound complex available for Ps formation, and I_3 decreases precipitously. On further increasing temperature (above T_β), because of the mobility of the matrix, the lifetime of free radicals and cations becomes shorter, i.e. the pool of available free radicals and cations which compete with Ps formation decreases, and the positronium formation probability begins to increase above T_β. When $T > T_g$, the lifetime of reactive species becomes too short to influence the Ps yield, thus a rapid increase of I_3 occurs on heating to 95°C (Fig. 3b). Clearly, at present, this hypothesis is based on limited observation, and needs to be supported by other measurements to probe radical and cation formation using independent techniques.

Above, we alluded to the fact that a minimum in o-Ps intensity I_3, and a decrease with the irradiation time, was also observed for high-density polyethylene (HDPE) in the rubbery state [12]. It seems unlikely that a similar explanation can be offered for this observation, since molecular mobility is exceedingly high. Instead, the changes in I_3 may be due to an irradiation-induced structural change. In support of this, we find a quite different behaviour of I_3 for a HDPE specimen subjected to a heating–cooling cycle. As

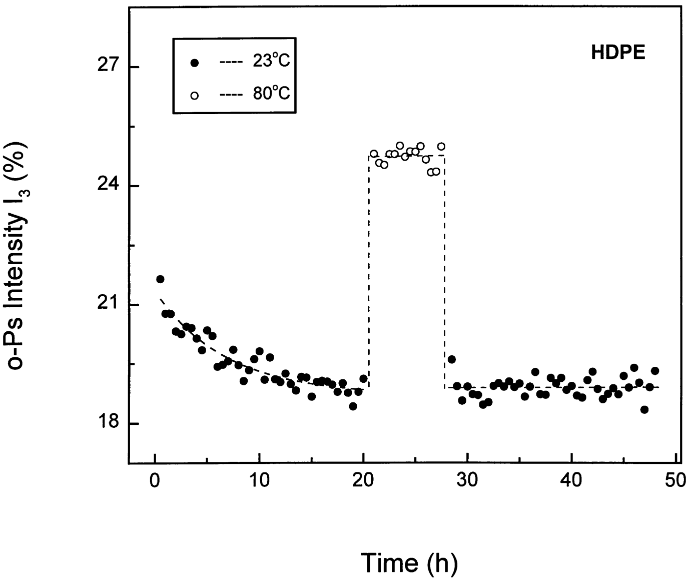


Fig. 4. Irreversibility of the e$^+$-irradiation damage in polyethyene.

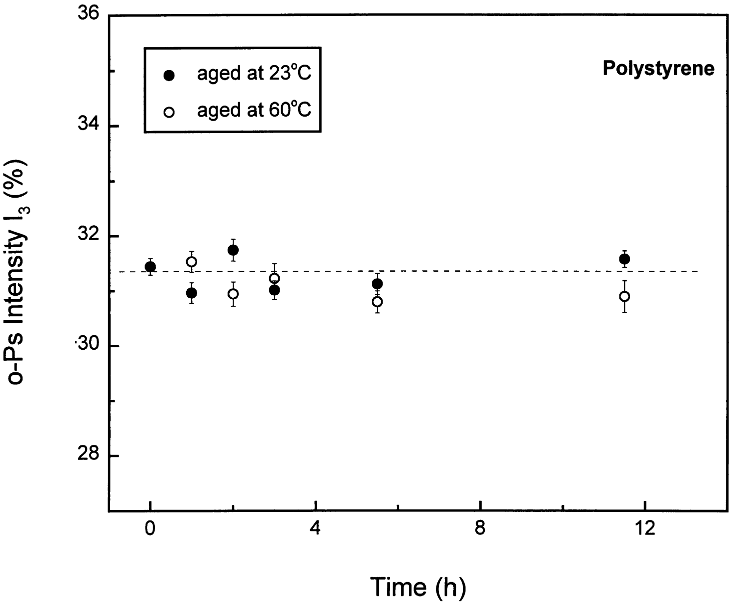


Fig. 5. Time dependence of the o-Ps intensity I_3 at 23 and 60°C after minimizing the contribution from e^+-irradiation damage.

shown in Fig. 4, upon exposure to e^+-irradiation at 23°C, there is a gradual decrease in o-Ps intensity I_3 to a steady-state value over a 20 h period. On increasing temperature to 80°C, I_3 immediately recovers to a constant (equilibrium) value. In contrast to the behaviour in polystyrene (Fig. 3b), on quenching from 80 to 23°C, I_3 instantly reverts to the steady-state damaged value before heating. In the irradiation of HDPE, free radical formation can lead to cross-linking between chains. Such radiation-induced cross-linking of polystyrene is difficult because of its aromatic units. Thus, in HDPE, it appears possible that a permanent change is produced in the vicinity of the radiation spur because of cross-linking of the matrix.

In previous studies, a decrease of I_3 with annealing in the glass has been observed and interpreted to be a result of structural relaxation of the polymers. To maximize the contribution from free volume relaxation, and minimize that due to e^+ exposure time, we investigated positronium decay in samples rejuvenated at 95°C for 30 min and subsequently aged at 23 and 60°C, in each case taking measurements at 23°C (cooling rate approximately 10°C/min). During these thermal treatments, samples were separated from the positron source. Fig. 5 shows the results for polystyrene. Clearly, the values of I_3, as well as the corresponding values of τ_3, show no significant aging effect. It is inferred that changes seen in Fig. 1b in the o-Ps yield are due to the radiation damage rather than a measure of changes in the void structure. Rejuvenation above T_g effectively erases the radiation damage in polystyrene, and the measured temperature dependence of I_3 approaches the value reflective of the number of free volume cavities. It should be noted that, if identical procedures to that in Fig. 4 are carried out via annealing at temperatures in the glass close to T_g, it may be possible to identify time-dependent changes in I_3 and τ_3 associated with relaxation of free volume [22,23].

4. Conclusion

We performed positron lifetime measurements to study the o-Ps formation probability in polystyrene as functions of temperature and time under isothermal conditions. While no deviation among the samples with different thermal history could be observed in the o-Ps lifetimes, the corresponding intensities were influenced by the thermal treatment of the samples, showing a minimum in I_3 near the β-transition temperature in samples subjected to sequential heating and cooling steps in the glass, and no such minimum in samples rejuvenated above T_g between each measurement in the glass. A decrease in the o-Ps intensity with e^+-irradiation time was observed whose rate is maximal near T_β. Temperature-jump experiments suggest that the minimum is due to the activation of reactive species near T_β which compete with Ps formation for electrons produced by energetic e^+ in the positron spur. Temperature jump experiments further confirm that the decrease in I_3 observed in glassy polymers on e^+-irradiation has a different mechanistic origin from that observed in polyethylene on irradiation above T_g. To identify changes in o-Ps annihilation parameters associated with changes in free volume during the physical aging process it will be necessary to carry out annealing treatments in the absence of the positron source.

Acknowledgements

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