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Positronium yields in amorphous, cross-linked and conductive polystyrene

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Abstract

Variations in positronium yields due to positron irradiation of specimens during experiment were investigated on the three commercially available modifications of polystyrene (Goodfellow): amorphous, cross-linked and conductive. Positron lifetime technique was employed. The variations of the positronium yields were expressed as changes of the ortho-positronium intensity as functions of the irradiation time. It was found that the positronium yield curves obtained for the amorphous and cross-linked polystyrene cannot be represented as a simple single-exponential relaxation towards a steady state and at least one additional component or a modified shape of the relaxation curve should be considered.

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1. Introduction

Positronium (Ps) is formed in a number of polymer materials exposed to irradiation by energetic positrons. Positronium exists in the singlet or triplet spin states—the *para*-positronium (*p*-Ps) and *ortho*-positronium (*o*-Ps), respectively (Mogensen, 1995). The singlet and triplet states are formed in the ratio of 1 : 3 (Goldanskii, 1968) and the self-annihilation lifetimes in vacuum are 0.125 and 140 ns for the *p*-Ps and *o*-Ps, respectively (Mogensen, 1995; Goldanskii, 1968). In condensed media, Ps can annihilate via the pick-off process in which an electron of the medium, forming the singlet pair with the positron, is involved. The pick-off process may reduce the *o*-Ps lifetime in the medium down to a value of ≈ 1 ns. The Ps formed in a polymer is repelled

into a free-volume hole and the observed *o*-Ps lifetimes, τ_{o-Ps} , were found to be well-correlated with the size of free-volume holes (Eldrup et al., 1981; Nakanishi and Jean, 1988; Ito et al., 1999).

Interpretation of the intensity of the *o*-Ps component, I_{o-Ps} , in the positron lifetime (PL) spectrum is not straightforward. Since I_{o-Ps} reflects the Ps formation probability, it is influenced by (i) the number of available free-volume holes in the polymer studied, (ii) the physical and chemical structure inherent to the polymer, (iii) the environmental parameters, like e.g., temperature, atmosphere, (iv) structural changes due to irradiation of the specimen by positrons from the positron source during the measurement. The last item lead to a commonly observed decrease of I_{o-Ps} in some polymers with the elapsed experiment time, T_{irr} . The first report on such a decrease came from Welander and Maurer (1992). Since that time, several mechanisms have been suggested to explain this kind of variations in I_{o-Ps} : structural relaxations (Welander and Maurer, 1992),

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irradiation induced electric fields (Qi et al., 2001), cross-linking (Badia and Duplaitre, 1999) and free radicals (Suzuki et al., 1995; Wang and Wang, 1997; Peng et al., 1999). Possible influence of the oxygen on observed I_{o-Ps} 's has also been considered recently (Suzuki et al., 2003). Irradiation of polymers with the energetic positrons (several hundreds of keV) leads to a production of positively charged radicals and other species that can reduce the Ps formation (Mogensen, 1995). In glassy polymers, these species may exhibit a substantial lifetime and, hence, a competition between the creation and recombination of these species occurs. This competition should lead to a relaxation of I_{o-Ps} towards an equilibrium stage when T_{irr} is extended and thus an exponential character of the relaxation is expected. It seems obvious, however, that the above listed mechanisms can act simultaneously with different characteristic times and the observed evolution of I_{o-Ps} with T_{irr} represents a fairly complicated phenomenon which is only roughly understood yet.

In the present work, PL spectroscopy has been applied to characterize detailed shape of variations of I_{o-Ps} with T_{irr} on a model polymer system. Polystyrene (PS) was chosen as the model system, because it is known from the previous works (Qi et al., 2001; Wang and Wang, 1997; Peng et al., 1999) to exhibit perhaps the largest effects of I_{o-Ps} decrease with T_{irr} . In order to elucidate the role of the inherent structure of the polymer, the three different structural modifications of PS were studied: amorphous, cross-linked and conductive PS.

2. Experiments

Specimens: The three PS modifications were purchased from Goodfellow: the amorphous (PS-A), cross-linked (PS-X) and conductive (PS-C) polystyrene. The specifications of these materials are given in web site (Goodfellow, 2005). The materials were supplied in the form of sheets of 2, 2 and 1.6 mm thickness, respectively. Specimens of the area of $13 \times 13 \text{ mm}^2$ were cut from the sheets. All the materials were studied both 'as received' (i.e., after 6 months of aging at ambient temperature in air), as well as after being subjected to an initialization annealing at 105–115°C for 1 h in dry nitrogen atmosphere.

Apparatus and data analysis: Two BaF_2 lifetime spectrometers were employed exhibiting a time resolution of 170 and 210 ps (FWHM) for ^{22}Na and count rates of 120 and 400 coincidence events per second, respectively. The spectrometers setup as well as data acquisition system were similar to that described in Becvar et al. (2000). Measurements were performed in air at an ambient temperature. The range of start–stop delays amounted 25 ns (3 ps/channel). The total time of

measurements (the maximum irradiation time) amounted typically 200–250 h. In order to follow the evolution of the o -Ps yields as a function of specimen irradiation time, the partial lifetime spectra were recorded in 1800 s steps. The spectra were decomposed into the three or four discrete exponential components using a maximum likelihood procedure (Procházka et al., 1997). Program LT (Kansy, 1996) was also employed to study continuous lifetime distributions.

3. Results and discussion

Measured PL spectra could be decomposed into the three discrete components exhibiting lifetimes of $\tau_1 \approx 0.16$, $\tau_2 \approx 0.4$ and $\tau_3 \approx 2.1$ ns. It has resulted from this analysis, that the three PLs appeared to be independent on the positron irradiation time T_{irr} . Such a behavior is a common observation on the amorphous polymers investigated by PL spectroscopy, in particular, it was found in previous measurements on PS (Qi et al., 2001; Peng et al., 1999; Li and Boyce, 1993; Dlubek et al., 1996).

The third component clearly represents a contribution from the o -Ps pick-off annihilations. In Table 1, the o -Ps lifetimes observed in the present work were summarized. The lifetimes obtained in the discrete analysis by averaging over the individual 1800 s runs are shown in the second column of the table. In the third and fourth columns of the table, the means and width parameters σ of τ_{o-Ps} distributions obtained by applying the LT program (Kansy, 1996) on the sums of the individual runs are presented. The o -Ps lifetimes revealed by the two approaches mutually slightly differ: the lifetimes from the continuous analysis are by ≈ 50 ps lower, however, the relative changes observed for different specimens are exactly reproduced by both the approaches.

Initialization annealing caused only minor influence on the o -Ps lifetimes (an increase by about 20 ps, see Table 1). The o -Ps lifetimes obtained in the present work

Table 1
The o -Ps lifetimes

	Discrete analysis	Continuous analysis (LT code)	
	τ_{o-Ps} (ns)	mean τ_{o-Ps} (ns)	σ (ns)
PS-A as received	2.023(5)	1.986	0.32
PS-A annealed	2.042(5)	2.008	0.32
PS-X as received	2.070(5)	2.033	0.32
PS-X annealed	2.079(5)	2.048	0.31
PS-C as received	2.133(5)	2.077	0.39
PS-C annealed	2.153(6)	2.106	0.39

for the amorphous PS are in a reasonable agreement with the previous results (Qi et al., 2001; Peng et al., 1999; Li and Boyce, 1993; Dlubek et al., 1996). For the cross-linked PS, a 40 ps increase in the τ_{o-Ps} compared to the amorphous one was detected (see Table 1). Actually, an increase of the average free-volume hole size in the cross-linked polymer may occur as a consequence of a less-ordered packing of chains compared to the uncross-linked one (Rey et al., 2004), however, the observed differences in τ_{o-Ps} are very small. The conducting PS is a high-impact PS with carbon filler (Goodfellow, 2005). The observed higher mean value and a remarkably broader distribution of τ_{o-Ps} is likely a consequence of an elastomer added to the material (Goodfellow, 2005).

The ortho-positronium intensities, I_3 , were followed as functions of T_{irr} in the intervals ranging from $T_{irr} = 0$ up to 150–200 h. Resulting $I_3(T_{irr})$ dependences for the specimens of as received materials are shown in Fig. 1. Exactly the same shapes of the $I_3(T_{irr})$ curves were obtained also for the annealed specimens. The intensities I_3 vs T_{irr} were yet measured only for the amorphous PS in the previous works (Qi et al., 2001; Wang and Wang, 1997; Peng et al., 1999; Li and Boyce, 1993; Dlubek et al., 1996). Thanks to an increased statistical accuracy, a more detailed information about the shapes of the measured dependences could be revealed in the present work. For the PS-A and PS-X, I_3 -values show a remarkably fast decrease within the first few hours of experiments, then I_3 decreases roughly exponentially at a moderate rate and, eventually, a much slower and almost linear decrease is seen in Fig. 1. It is evident that the evolution of I_3 with T_{irr} cannot be reduced simply to a single mechanism of a competition between the creation and decay of free radicals, as considered in Wang and Wang (1997). We therefore attempted to parametrize the measured dependences

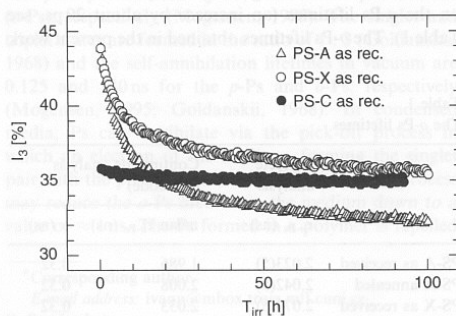


Fig. 1. A comparison of the measured dependences of the *o*-Ps intensity, I_3 , on the positron irradiation time, T_{irr} for the three modifications of polystyrene.

with the expression

$$I_3(T) = b_1 \exp(-\lambda_1 T) + b_2 \exp(-\lambda_2 T) + aT + c, \quad (1)$$

where b_i , λ_i ($i=1,2$), a and c are the variable parameters which were determined by a least square fit to experimental data. The results of such fits were summarized in Table 2 and an example of the fit is given in Fig. 2. Within this parametrization, the evolution rates of I_3 with T_{irr} can be characterized with relaxation times of ≈ 4 and ≈ 25 h, see Fig. 2 and Table 2. In the course of the present work, the paper (Djourelou et al., 2003) appeared in which a two-component relaxation with characteristic lifetimes similar to the present findings was reported on polypropylene. In addition, a very slowly decreasing component was observed in the present work.

As can be seen in Fig. 1, the curve for PS-C remains almost constant with increasing T_{irr} . This feature is different from the PS-A and PS-X specimens. Obviously, it should be regarded as a consequence of a much higher conductivity of PS-C (Goodfellow, 2005), compared to the PS-A and PS-X, which almost completely prevents accumulation of the irradiation induced charges and species that would normally decrease the Ps formation probability. A remarkably lower value of I_3 at $T_{irr} = 0$ with respect to the PS-A and PS-X was observed for

Table 2
Parametrization of the observed dependences $I_{o-Ps}(T_{irr})$ by fitting expression (1) to the experimental data

	b_1 (%)	λ_1 (h ⁻¹)	b_2 (%)	λ_2 (h ⁻¹)	a (h ⁻¹)	c (%)
PS-A as received	6.5	0.24	4.7	0.052	-0.023	33.4
PS-A annealed	7.8	0.33	4.2	0.046	-0.025	31.8
PS-X as received	4.4	0.26	3.0	0.049	-0.026	36.8
PS-X annealed	7.3	0.34	1.5	≈ 0.03	≈ 0.02	34.9

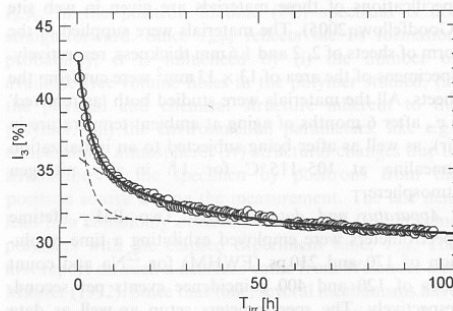


Fig. 2. The fit of expression (1) to the experimental curve $I_3(T_{irr})$ for the annealed PS-A: open circles—experimental data, solid line—fitted I_3 -values, dashed lines—individual exponential and straight-line components.

