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POSITRON IRRADIATION EFFECTS ON POSITRONIUM FORMATION IN POLYCARBONATES DURING A POSITRON-ANNIHILATION EXPERIMENT

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The positron-irradiation effect on polycarbonate during a positron-annihilation lifetime spectroscopy experiment was investigated using different intensities of ^{22}Na positron sources and γ-irradiated samples. The decrease in I_3 was larger for a larger intensity of positron sources. In the case of a weak source ($\approx$ 140 kBq), I_3 did not change with the elapsed time for non-irradiated samples. However, for 1 MGy irradiated samples, I_3 measured with the weak source increased with the elapsed time. This can be attributed to a decrease in the radicals induced in the irradiated samples by γ-irradiation. In order to explain the change in I_3 measured at room and liquid-nitrogen temperatures, several effects, such as radicals, cross-linking, structure change, and charging, need to be considered. Also, it is difficult to explain the change in I_3 using only one of these effects.

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1. Introduction

The positron-irradiation effect has been discussed and increases and decreases in the positronium (Ps) formation have been reported at low temperature [1–4] and room temperature [5–7], respectively. Before observing Ps quenching by irradiating polymer samples with visible light [8–10], the increase at low temperature was explained by the relaxation behavior of polymer structures. A quenching experiment has demonstrated that Ps formation is accelerated by an increase in the trapped electrons, which are induced by the ionization of injected positrons, which are trapped in a shallow potential being formed among polymer structures at low temperature [8–10]. This is a phenomenon similar to the well-known "anti-inhibition or anti-recombination effect" [11].

The decrease in I_3 at room temperature has been explained by many ideas, such as cross-links [12], structure change [13], and radicals [14]. A structure change and the cross-links were introduced to explain the decrease in I_3 at low γ-irradiation doses of around 10 kGy, since, at a low irradiation dose, it seems to be difficult to expect radicals which affect the change of I_3.

In this studies, the reduction of Ps formation has been explained using several effects, mentioned above, and the effect of positive charges, which constantly accumulate by injecting positrons in polymers from positron sources during PALS measurements.

2. Experiment

The PALS experiments were conducted using a conventional fast-fast coincidence system having a time resolution of 270–300 ps at full width at half maximum (FWHM). The details of the apparatus have been presented elsewhere [7].

The polycarbonate (PC) sample used in the experiment was commercially available from Sigma-Aldrich Japan K.K.; the sample was supplied in pellet form and was melted at 320°C to form a plate of 1–2 mm thickness. The plate was then cut into pieces of 10 mm × 210 mm for PALS experiments.

Positron sources were prepared by depositing and drying aqueous ^{22}NaCl on a 7 μm thick kapton film having an area of 10 mm × 10 mm, which was then covered with the same size of film. In order to investigate the dependence on the positron source, three kinds of sources with intensities of 3.7 (100), 0.96 (26), and 0.18 (5) MBq (μCi) were employed.

In order to study the effect of γ-ray irradiation, the PC samples were sealed in glass tubes under a vacuum and irradiated at room temperature at the ^{60}Co γ-ray irradiation facility, Japan Atomic Energy Research Institute (JAERI). After keeping the samples at room temperature for more than one week, they were used for PALS experiments, and the free radicals induced by the irradiation were measured by ESR (JEOL JES-RE3X). Hence, this work was concerned with long-lifetime free radicals.

The PALS spectra were automatically saved every one or two hours, resulting in 1 to 2 million events in each spectrum. All spectra were resolved into three components using the PATFIT program [15]; the longest lifetime component (intensity I_3, lifetime τ_3) was related to *ortho*-Ps (*o*-Ps).

3. Results and discussion

Polycarbonate has aromatic rings in the structure, which can absorb the energy of radiation, and the G value of scissions is known to be 10 to 50 times smaller than those of polyethylene [16, 17]. Hence, ionized electrons may be produced less efficiently than polyethylene by radiation. Generally, a PALS experiment is conducted by sandwiching the positron source between two polymer samples, which are continuously irradiated by the probe positrons, whose energy is distributed from 0 to 540 keV and the average energy is about 220 keV. From the irradiation, the maximum energy deposit was estimated to be about 400 Gy/h for a 3.7 MBq source in a small part located within 20 μm from the surface [18]; the accumulated dose within 1 h was sufficient to produce 10^{16}–10^{17} radicals/(g·h). Also, during the PALS experiments, positron probes were constantly adding positive charges to polymer samples, resulting in the accumulation of charge. Thus, radicals and positive charges were accumulating with the elapsed time of the PALS measurement.

Figure 1 shows the normalized I_3 versus the elapsed time during PALS experiments using three kinds of intensities of ^{22}Na sources for the non-irradiated

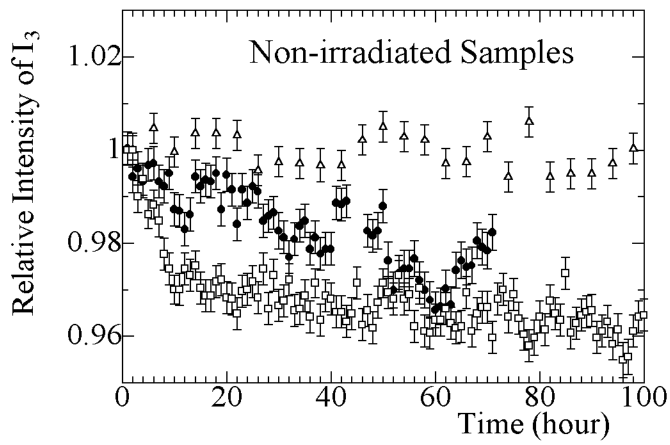

Fig. 1. Normalized I_3 versus the elapsed time for the non-irradiated PC samples during PALS experiments using three kinds of intensities of ^{22}Na sources: open triangle 0.18 MBq (5 μCi); solid circle 0.96 MBq (26 μCi); open square 3.7 MBq (100 μCi).

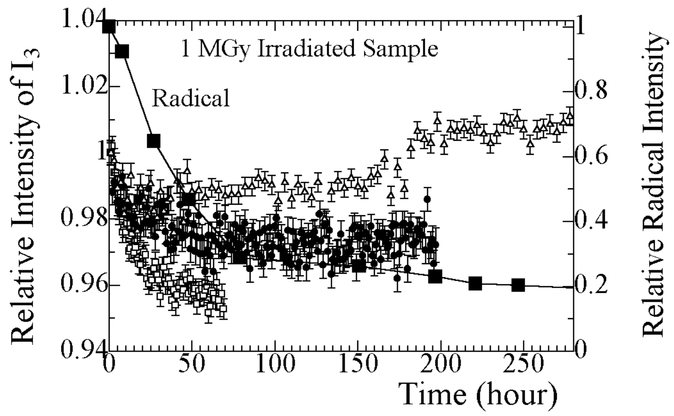

Fig. 2. Normalized I_3 and radicals (solid square) versus the elapsed time for 1 MGy irradiated PC samples; symbols are the same as listed in the caption of Fig. 1.

samples. In this experiment the positron sources were always sandwiched by two polymer samples, and the time of the x-axis shows both the elapsed time of the measurement and the irradiation time. It indicates that the decreasing rate of I_3 depends on the intensity of the source, and that no decrease is observed for the 0.18 MBq source (Fig. 1 shows up to 100 h). The same measurements were conducted using 1 MGy irradiated samples at the ^{60}Co γ-ray facility (JAERI); the decreasing rate also depends on the intensity of the source (Fig. 2). However, in the case of a weak source (0.18 MBq), I_3 seems to increase after 150 h of elapsed time. Figure 2 shows the relative radical intensities versus the elapsed time. Since, after 150 h, the radical intensity decreased to 20% of the initial value, the increase in I_3 after 150 h is considered to be attributed to a decrease in the radical density.

Figures 3 and 4 show I_3 versus the elapsed time measured using strong (3.7 MBq) and weak sources (0.18 MBq), respectively. I_3 of the non-irradiated sample was larger than that of 1 MGy irradiated samples by 3–4%. This may

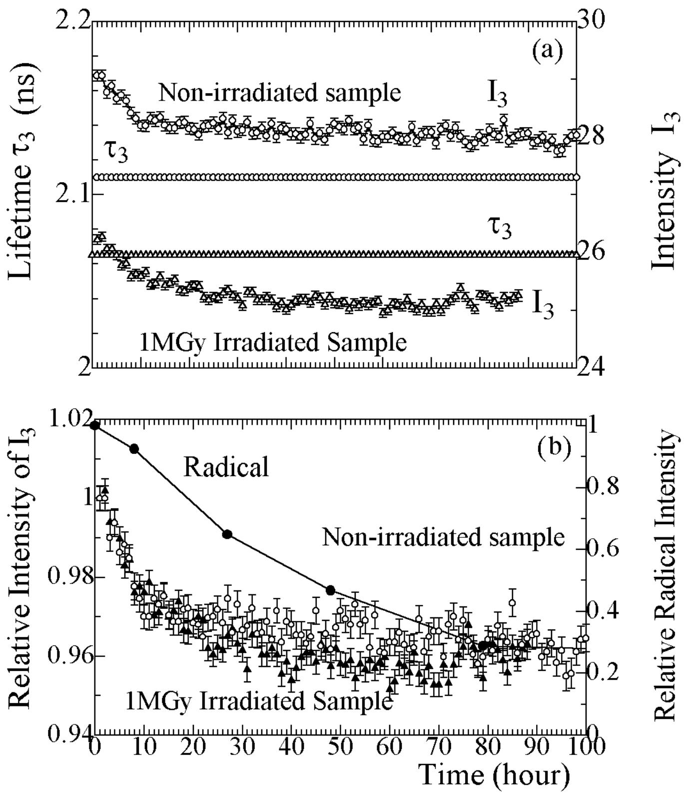

Fig. 3. (a) Lifetimes and intensities versus the elapsed time for the irradiated and non-irradiated PC samples using the strong source of 3.7 MBq during PALS experiments. (b) Normalized intensities and radicals for the data shown in part (a).

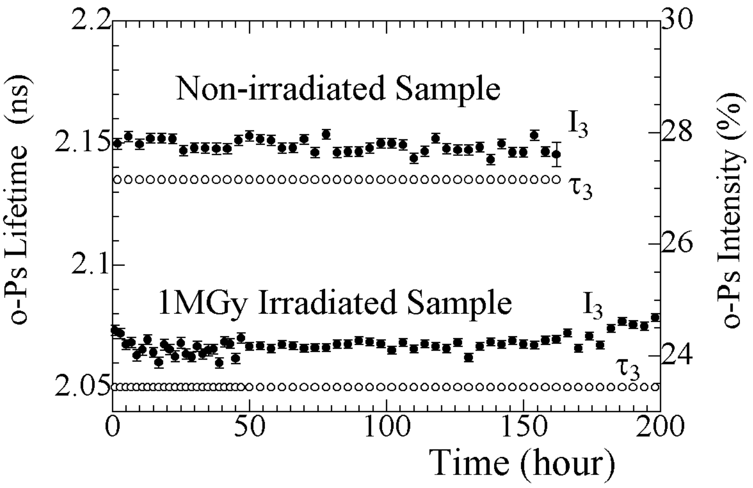

Fig. 4. Lifetimes and intensities versus the elapsed time for the irradiated and non-irradiated PC samples using the weak source of 0.18 MBq during PALS experiments.

be attributed to the radicals, since, in the 1 MGy irradiated sample, radicals of 3×10^{18}/g were observed even after more than one week. Also, τ_3 of the irradiated samples was smaller than that of the non-irradiated samples. This indicates that a structure change due to cross-linking occurred, and that the intermolecular spaces shrunk. Thus, the decrease in both I_3 andτ_3 can be attributed to radicals and cross-linking, which are generally expected to be induced in irradiated samples.

In the case of the strong source, the decreasing rate of I_3 for the 1 MGy irradiated samples was almost the same for the non-irradiated samples. If the cause of the decrease was due to radicals, the decreasing rate in the irradiated samples may not be the same as that of non-irradiated samples, since the number of radicals induced by the source at the beginning of the PALS experiment is smaller than the number of radicals existing before the measurement. Hence, the decrease in I_3 may not have been caused by radicals, and may be attributed to the accumulation of charges. After a 1 hour PALS measurement, the accumulation was estimated to form an electric field larger than 30 kV/cm, which is sufficient to affect Ps formation [11]. For a weak source, because I_3 does not change for non-irradiated samples, the effects of radicals and charges, which are induced by the positron source, may be small.

At low temperature, I_3 showed different variation from that at room temperature. For non-irradiated samples, Fig. 5 shows that I_3 began to increase as soon as the sample was cooled down to liquid nitrogen temperature. However, for the irradiated samples, I_3 decreased at the beginning, and then started to increase after 200–220 h. The increase in I_3 of non-irradiated samples can be explained by trapped electrons [8–10], which are trapped in the potentials created after the freezing of molecular motion, and can overcome the effects of radicals and charges in order to form Ps. Since the induced radical numbers and the charging effect should be similar in the irradiated and non-irradiated samples, the decrease in I_3

at the beginning of sample irradiation may be attributed to a smaller number of trapped electrons. This is due to the capture of ionized electrons by radicals being induced in the irradiated samples by γ-irradiation before a PALS measurement. Hence, if radicals are the main effect to Ps formation, I_3 cannot increase, and is also expected to be constant. However, I_3 decreases with the elapsed time of the PALS measurement. In order to explain this decrease, another effect, such as an electric field created by positive charges, must be introduced. Positive charges are constantly injected into samples from positron sources; also, through the capture of ionized electrons by radicals positive charges accumulate faster than charging from the sources.

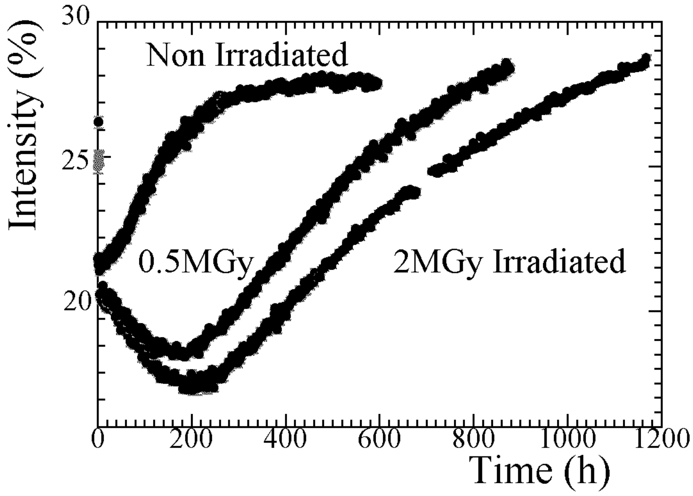

Fig. 5. *o*-Ps intensities versus elapsed time at the liquid nitrogen temperature for non-irrradiated, 0.5 MGy irradiated, and 2 MGy irradiated PC samples.

The charging effect has been considered as one of effects to reduce Ps formation [11, 19]. In our study, the effect can be estimated as follows. A positron source of 3.7 MBq emits half of the source activities (1.85 Me^+/s) towards one side of the samples. Half of these positrons are accumulated within a region covered by e^+ penetration — source diameter (2 mm) $\times$ depth (≈ 30 μm). Then the positron density can be estimated to be $\approx 3.5 \times 10^{19}$ $e^+/(h{\cdot}m^3)$ from the 3.7 MBq strong source. If these positrons are distributed uniformly, the distance between two charges is roughly 30 nm. If injected positrons locate 15 nm away from one positive charge, an electric field of 64 kV/cm is expected from one charge. This suggests that, since the electric field may become larger than 30 kV/cm, which was measured to affect Ps formation in nonpolar liquids [11], there is a large possibility to affect Ps formation.

4. Conclusion

In order to explain the change of I_3 during a PALS experiment, a charging effect due to positrons injected by the positron sources must be considered [11, 19] in addition to radicals, cross-linking, and a structure change. We observed that the decreasing rate of I_3 was the same for irradiated and non-irradiated samples in the PALS measurement using a strong source; also, during the beginning of the PALS measurement at the liquid temperature, I_3 decreased (increased) for irradiated (non-irradiated) samples. It seems that radicals, cross-linking, and structure changes cannot explain these changes of I_3.

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