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Radiation effect on polypropylene studied by the relaxational behaviour at low temperature using positron annihilation

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The irradiation effect of γ-rays on polypropylene (PP) has been studied through relaxational behaviour, using the positron annihilation lifetime (PAL) method. At low temperature, the intensity of a long-lived component of positronium, I_3, for unirradiated PP samples increased due to a termination of the local thermal motion of polymer structures. At 100 K, the increase in I_3 of 1 MGy γ-ray irradiated samples became very small. However, the increase was observed again in the PP samples after 48 h of irradiation by positrons during the PAL experiment. This suggests a restructuring of the short polymer chains cut by γ-ray irradiation may occur. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Positron annihilation (PA) in polymers has been extensively studied during the last decade, and the positron annihilation lifetime (PAL) technique has become recognized as a useful method for studying the characteristics of polymers[1–7], in which ^{22}Na positron sources are commonly employed. However, positrons emitted from the source have sufficient energy (average energy ~200 keV) to induce radiation effects on polymers, and the positron probe can thus affect the object being investigated during PAL measurements. It has been pointed out that the positron irradiation effect is quite significant when polyethylenes (PEs) and polypropylenes (PPs)[8–10] are used as samples.

It has been reported for PE that at low temperature I_3, a long-lived positronium (Ps) component, increases along with decreasing temperature, and that β-relaxation at 246 K and γ-relaxation at 200 K can be observed[11–13]. These relaxations are considered as follows: the former was associated based on micro-Brownian motion, and the latter based on a local thermal motion of polymer structures and short branches. When samples were quickly cooled from room temperature to 100 K, the increase in I_3 took a few days to reach a maximum, at which point the polymer structures were considered to obtain thermal equilibrium[5]. The time required to reach equilibrium is considered to be equivalent to the relaxation time of the polymer structures at low temperature. The time-dependent volume change (volume relaxation) for PE[14] has shown relaxation

times longer than 100 h to reach an equilibrium, when the sample was quenched from room temperature to 240 K. These experimental results suggested that the internal polymer structures may take a very long time to attain thermal equilibrium.

In this report, the radiation effects on PPs due to both positrons and γ-rays were investigated by the PAL method. Positrons emitted from positron sources play a role as probes for studying polymer structures and, at the same time, serve as radiation to induce radiation effects in samples.

Experimental

The PA experiments were conducted using a conventional fast-fast coincidence system having a time resolution of 270 ps full width at half maximum (FWHM). The details have been presented elsewhere[10].

Isotactic PP slabs (2 mm thick) were cut into pieces to an area of 10×20 mm^2: it has a crystallinity of 55%, which was determined by X-ray measurements, density 0.91 g cm^{-3}, a glass transition temperature (T_g) around 273 K, and melting point (T_m) around 433 K. The samples were kindly supplied by Mitsui Petrochemical Industries Ltd.

Positron sources were prepared by depositing *ca* 1 MBq on a 10×10 mm^2 area. After drying, the foil was covered with the same size of foil; the edge was then glued with epoxy resin. For PA experiments, the positron source was sandwiched between two pieces of PP sample. Each PA spectrum was automatically saved every hour, resulting in 2 million events being collected in each spectrum.

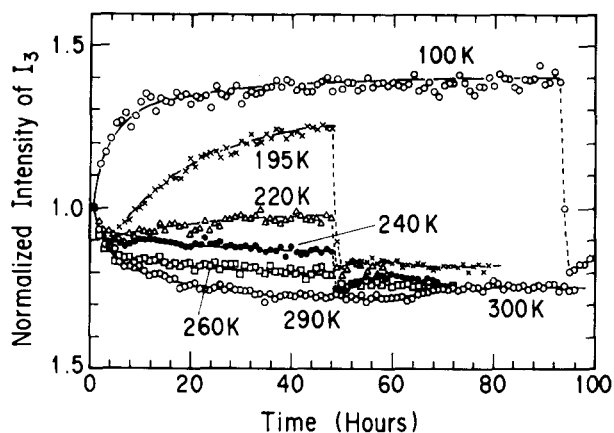* To whom correspondence should be addressed

Figure 1 Normalized intensity of I_3 vs time for polypropylene. The data were normalized to the first 1-h data, which were taken at 300 K. The samples were kept for 48 h at 190–260 K and 93 h at 100 K. Since it took 40 min for samples to be cooled to 100 K, the second data set includes the temperature transient effect from 300 K to the target temperature

Figure 2 Radiation effects on the increase in I_3 at 100 K. The samples were irradiated by [60]Co γ-rays

The PA spectra were analysed using Positronfit Extended[15]. In polymers, three lifetime components are commonly observed. For PP and PE, four components can be deduced with good statistics[11]: two long-lived components (lifetime τ; 1–3 ns) originate from *ortho*-Ps, the shortest one (τ; 0.1–0.2 ns) from *para*-Ps and the intermediate one (τ; ~0.4 ns) from the free positrons. In this experiment, each spectrum had two million events and the statistics were not good enough to deduce the four components reliably. Especially at low temperature, the difference between lifetimes of the two long-lived components was so small that the four component analysis became difficult. Hence all spectra were analysed with three components: only the longest lifetime component (I_3) was related to *ortho*-Ps.

In order to study the effect of γ-ray irradiation, the samples were sealed in glass tubes under vacuum and irradiated at room temperature at the [60]Co γ-ray irradiation facility, Japan Atomic Energy Research Institute (JAERI).

Results and discussion

Temperature dependence on positronium formation. Figure 1 shows I_3 for seven different temperatures: for 100 K, the sample temperatures were restored to 300 K after 93 h; for the other low-temperature cases, it was after 48 h. The results indicate the following: (1) the lower the sample was cooled, the more I_3 increased; (2) as soon as the temperature was restored to 300 K, I_3 reached the same value as that of samples irradiated at 300 K; (3) as shown before by Walender and Maurer[8], I_3 decreased with the irradiation time at around room temperature.

The increase in I_3 at low temperature has been demonstrated in polyethylenes[5,6] and in paraffins[16], which is explained in the references as follows: (1) the local hindered rotational motions of side and end groups are frozen; (2) under the frozen structure, both electron mobility and electron density distribution increase in the lattice and decrease in the holes, resulting in the increase in I_3; (3) in polyethylene, because of the different thermal expansion coefficient in the amorphous and crystalline region, stress is induced, resulting in additional inter-
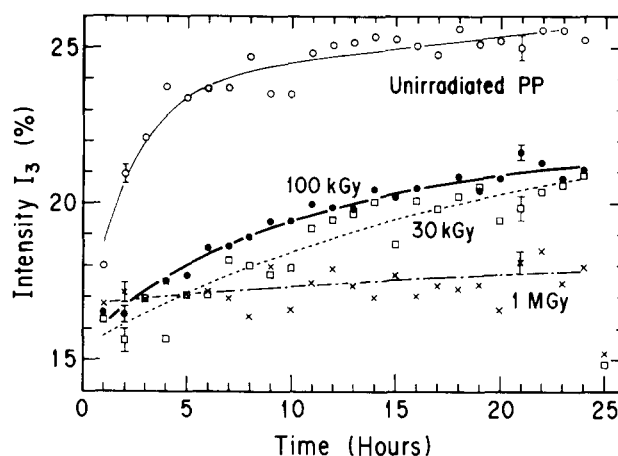
molecular-space holes; (4) the preexisting holes blocked by local molecular motions are accessible due to the loss of screening effect under the freezing of the local thermal motions of polymer structures and short branches.

In polymers like PE and PP, Ps formation is expected to increase in proportion to the numbers of intermolecular space holes in which Ps can be trapped, since these sample do not have any chemical groups with strong electron affinities in the chemical structures. If there are chemical groups in the polymer structures such as carbonyls, Ps formation is strongly reduced, especially at low temperature. This was demonstrated by the thermal oxidation experiment of PE: carbonyl groups were formed in samples to inhibit Ps formation through trapping the precursors (e^+ and/or e^-) of Ps[13]. If there is no effect due to the local thermal motions of polymer structures, I_3 should decrease in these samples with decreasing temperature, because the intermolecular space holes become small and Ps cannot be trapped any more in the small holes, i.e. the decrease in the number of holes for Ps. However, many experiments[11–13] have shown an increase in I_3 at low temperature and hence the structure effect caused by decreasing temperature was considered to be significant.

In order to investigate what kind of thermal motion is involved, the γ-relaxation temperature at 200 K for PE observed by PA is important: it is equivalent to that of dielectric relaxation of local thermal motions of PE for a low frequency around 1 Hz or less[17]. If dipole moments have a motion in polymer structures, Ps formation is expected to be reduced, and hence I_3 is expected to increase following dielectric relaxation. Since no electric field was applied from outside during the PA measurements, the relaxation related to the Ps formation is considered to be that of low frequency.

Positron annihilation in γ-ray irradiated samples. PAL measurements of PP samples irradiated by γ-rays of ^{60}Co were conducted in a vacuum at 100 K for 24 h; the time variation of I_3 is shown in *Figure 2*. The samples were cooled from room temperature to 100 K within 40 min, and, thus, the first hour data show I_3 during the temperature variation from room temperature to 100 K. Although a sharp increase in I_3 was observed for unirradiated samples, the increase became smaller in
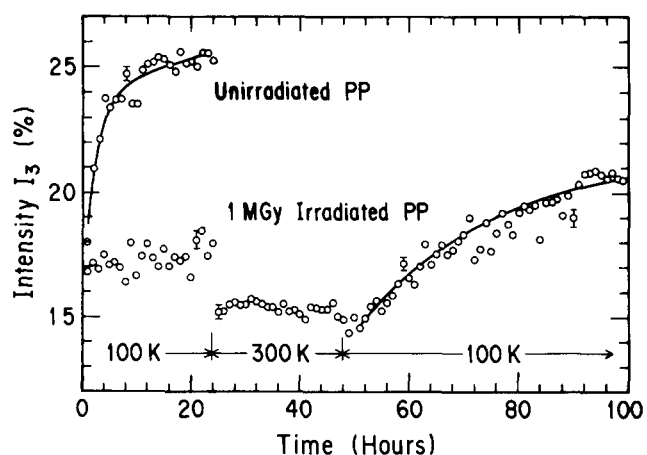
Figure 3 Positron irradiation effects on polypropylene irradiated by ^{60}Co γ-rays. The increase in I_3 for the unirradiated samples is shown for a comparison with that of the irradiated one for the first temperature region. At the second cooling at 100 K after 48 h, an increase in I_3 appeared, again due to positron irradiation

those samples irradiated with a larger dose; it was almost negligible for 1 MGy irradiated samples. Since the increase has been explained in terms of the termination of local thermal motions of polymer structures or short branches along rigid polymer structures, the negligible increase observed at higher irradiation may suggest the loss of rigid polymer structures due to radiation induced scissions. Hence, it is considered that, in the γ-irradiated samples, short polymer structures can attain equilibrium quickly due to the loss of the stiffness of the polymer structures.

Restructuring effect on γ-ray irradiated samples. *Figure 3* shows both the position and γ-ray irradiation effects in the following three temperature regions for a γ-ray irradiated sample: (1) 0–24 h, 100 K; (2) 25–48 h, 300 K; (3) 49–100 h, 100 K. Although I_3 for an unirradiated sample increased sharply in the first region, I_3 for the 1 MGy irradiated sample with γ-rays showed a negligible increase, and was almost constant for 24 h. In the second region, I_3 became smaller than that in the first region and the value at 25 h was almost the same as that obtained after 25 h of positron irradiation at room temperature, which is consistent with the results of *Figure 1*.

The increase in I_3 can be fitted by the equation $1 - \exp(-t/T)$, where t is the positron irradiation time in hours and T a constant, which may be equivalent to the relaxation time related to the thermal motions of the local polymer structures. As soon as samples are cooled from 300 to 100 K, polymer structures are considered to relocate the three-dimensional configuration in order to obtain thermal equilibrium with the relaxation time (T). T may indicate the characters of stiffness for relocation of the main structures and branches, where Ps is trapped.

For the unirradiated case, two Ts, $T_1 = 3$ h (fast component) and $T_2 = 20$ h (slow component), were obtained, as expected, from the graph. If there are a sufficient number of events to fit the PAL spectra with four components, two long-lived components can be found in the case of PP: one is due to Ps formed in the crystalline region; the other is due to that in the amorphous region. In our case total events were insufficient to deduce four components as stated in the Experimental section. In the previous study[11], the time

variation of the longest lifetime component (Ps in the amorphous region) was obtained with sufficient statistics, which showed a relaxation time of about 20 h. Hence, the T_2 shown above for an unirradiated sample is considered to be equivalent to the relaxation time in the amorphous region and T_1 in the crystalline region.

In the third region, a gradual increase in I_3 was observed for the 1 MGy γ-ray irradiated samples. The relaxation time obtained for the increase was determined to be 28 h, and no fast relaxation time was obtained. Hence, the relaxation time indicates that Ps was formed in a structure similar to the amorphous region, which had not been observed at the beginning of the experiment for the γ-ray irradiated samples. This can be explained as follows: as soon as the samples were warmed to 300 K in the second region, radicals created and frozen at 100 K in the first region could move freely, resulting in cross-linkings of broken chains.

Conclusions

Positron annihilation has been applied to the relaxational behaviour of PP at low temperature. Using positron sources for positron annihilation experiment, positron irradiation effects on γ-ray irradiated PP have been studied through relaxational behaviour.

The increase was fitted with two components of the relaxation time; the slow component was considered to be related to the amorphous region. Our results suggest that the relaxation time of local polymer structures in the crystalline regions is shorter than that in the amorphous regions. The local thermal motions can thus obtain thermal equilibrium quickly in the crystalline region.

Although the increase in I_3 was not observed for the 1 MGy γ-ray irradiated samples during the first stage of cooling at 100 K, the increase appeared during the second stage of cooling after heating the samples to room temperature. From the relaxation time, the structure similar to the amorphous region was considered to be reconstructed, suggesting positron-induced cross-linkings of broken polymer structures caused by radiation-induced scissions.

References

1   Jean, Y. C. *Microchem. J* 1990, **42**, 72
2   Suzuki, T., Oki, Y., Numajiri, M., Miura, T., Kondo, K. and Ito, Y. *J. Appl. Polym. Sci.* 1993, **49**, 1921
3   Billard, I. (Ed.) *J. Phys. IV* 1993, **3**, Suppl. JP II, 9 (and refs therein)
4   Proceedings of the 10th Int. Conference on Positron Annihilation (ICPA10), 23–29 May, 1994, Vols 175–178, Beijing, China, Materials Science Forum, 1995
5   Mogensen, O. E. 'Positron Annihilation in Chemistry', Springer, Berlin, 1995
6   Schrader, D. M. and Jean, Y. C. (Eds) 'Positron and Positronium Chemistry', Amsterdam, 1988
7   Ito, Y., Kaji, H., Tabata, Y. and Yoshihara, K. 'Chemistry of Elementary Particles (Soryushi no Kagaku)' (in Japanese), Gakkai Shuppann Center, Tokyo, 1985
8   Walender, M. and Maurer, F. H. J. *Mater. Sci. Forum* 1992, **105–110**, 1811
9   Suzuki, T., Oki, Y., Numajiri, M., Miura, T., Kondo, K. and Ito, Y. *J. Phys. IV* 1993, **3**, 283

10 Suzuki, T., Oki, Y., Numajiri, M., Miura, T., Kondo, K. and Ito, Y. *Radiat. Phys. Chem.* 1995, **45**, 657
11 Reiter, G. and Kindl, P. *Phys. Stat. Solids (a)* 1990, **118**, 161
12 Zhang, Z. and Ito, Y. *Radiat. Phys. Chem.* 1991, **38**, 221
13 Suzuki, T., Oki, Y., Numajiri, M., Miura T., Kondo, K., Shiomi, Y. and Ito, Y. *Radiat. Phys. Chem.* 1994, **43**, 557
14 Davis, G. T. and Eby, R. K. *J. Appl. Phys.* 1973, **44**, 4274

15 KirKegaard, P. and Eldrup, M. *Comput. Phys. Commun.* 1974, **7**, 401
16 Levai, B., Lalovic, M. and Ache, H. J. *J. Chem. Phys.* 1989, **90**, 3282
17 Wada, Y. 'Solid Properties of Polymers' (in Japanese), Baihukan Co., Tokyo, 1971