Positron Annihilation in Radiation-induced Solid State Polymerization

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This paper deals with positron annihilation in the system of irradiated monomers where the radiation-induced polymerization is taking place in solid state. If positrons are emitted in this system, the active species accumulated by irradiation with γ-ray would interact with positroniums formed in the system in such a way that: 1) triplet to singlet conversion originating from unpaired electron spins, 2) capture of positronium atom by active species in the system. As a result, either the shortening of the long lifetime of positrons (τ_2) or the decrease of its intensity (I_2) would be caused.[1,2] Moreover, the crystalline structure of monomer changes with the formation of polymers, and the amount of defects and dislocations increases with polymerization. Positronium can stay comparatively longer in such deformed lattices, and then the pick-off rate of positronium would be decreased, resulting in the lengthening of τ_2.[3] This method has been tried to apply to several polymerization systems in solid state in our laboratory.[4] Among these experiments, solid state polymerization of acetaldehyde is reported here. It was distilled in vacuum into a glass ampoule containing the positron emitter $\sim 5\mu$Ci ^{22}NaCl. Irradiation for the polymerization was carried out by a ^{60}Co γ-ray source. Dose rate was $\sim 10^4$ R/hr.

The lifetime measurements were made by a conventional fast-slow coincidence system, with MBlO plastic scintilators, 56AVP photo-multipliers, a Weisberg-type time to amplitude converter,[5] and TMC 100 channel analyzer. The resolving time obtained with γ-rays from a ^{60}Co source was 0.9 nsec. The accumulated data were analyzed by a HITAC 5020A computer.

These results are given in Fig. 1. The lifetime spectrum of an irradiated sample, where more than 30 wt% of monomer is estimated to have been converted to polymer, seems not to have any longer tail components at -196°C. This spectrum is similar to that of an unirradiated sample.

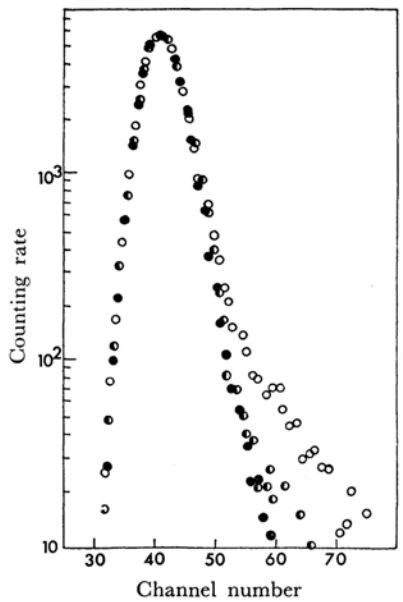

Fig. 1. Positron lifetime spectra in acetaldehyde at -196°C. (0.20 nsec/channel)
●: Irradiated for 3 hr
◑: Kept at -130°C for 30 min
○: Kept at room temperature for 30 sec

After this measurement, the sample was kept at -130°C (just below the melting point of acetaldehyde: mp -123.5°C) for 30 min. After cooling down of the irradiated monomers, the lifetime spectrum was measured again at -196°C. A long tail component appeared in the lifetime spectrum at -196°C. The lifetime τ_2 was 1.10 nsec and I_2-value was 7%.

Then the sample was warmed up to room temperature and immediately cooled down to -196°C. The lifetime spectrum of this sample which dose not include any radicals, has now the longest τ_2 (1.68 nsec) and the largest I_2 (12%) among three different conditions.

Thus it was shown that the positron lifetime spectrum was affected by both lattice deformation due to polymerization and accumulation of active species with irradiation. However, it was suggested to be possible to distinguish both effects by treatments of the irradiated monomers under various conditions after irradiation. One can say that the variation of positron lifetime spectra by irradiation give useful informations about the mechanism of solid state polymerization.

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