Positron-lifetime Measurements in Polymerizing Organic Solids

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The measurement of the e^+ lifetime in solid monomers during polymerization has been carried out. The mechanism of solid-state polymerization can be analyzed by the measurement of the lifetime of positrons and the amounts of positronium formed. This method was applied to the solid-state polylmerization of acrylamide. It was found from the experiments that the lifetime spectrum changes remarkably in the induction period of polymerization. The decrease in the annihilation rate λ_2 was interpreted in terms of the formation of a larger free volume during polymerization. The intensity of the slow component was also observed to decrease in the induction period of polymerization. The accumulation of active species which capture positrons and the decrease in the number of free volumes were suggested as explanations of the phenomena.

During the last 20 years, the positron annihilation in matter has been studied extensively, and most of the experimental results have been collected.[1-3] Although the experimental data have as yet a qualitative character, it is expected that positron annihilation can be used as a probe in the study of solid materials. A positron can capture an electron in a medium in which it is slowing down, and form a bound state which is called positronium (Ps). There are two ground states of Ps: the triplet state Ps, with total spin $S=1$, and the singlet state Ps, with total spin $S=0$. The lifetime of the singlet Ps (s-Ps) is so short ($\tau=0.125$ nsec) that its component is not separable from the component of the free annihilation of positrons in condensed media. The intrinsic lifetime of the triplet Ps (t-Ps) is 140 nsec, but the lifetime is considerably reduced in condensed media, since t-Ps can possibly be annihilated with electrons of the surrounding molecules *via* the following several processes:

(1) The e^+ in t-Ps can sample electrons of the surrounding molecules and be annihilated rapidly. This process is called "pick-off" annihilation. The lifetime is related to the size of the free volumes in which t-Ps can reside. The smaller the free volume in a medium, the shorter the lifetime of t-Ps.[4,5]

(2) If t-Ps can react with impurities in the medium and form a bound-state "positronium compound", the lifetime of t-Ps is reduced, because the positron is situated in a dense electron cloud and may be annihilated rapidly.[6]

(3) If the impurity molecule has an unpaired electron, t-Ps is converted into s-Ps upon collision with it and is annihilated rapidly. This process is called "triplet-to-singlet conversion" or "exchange collision." Most of the annihilation by these processes is followed by the emission of two photons of 0.51 MeV in opposite directions.

In most organic solids, the lifetime spectrum of positrons is composed of two or three components. The slow component of the lifetime spectrum may, in general, be attributed to the decay of t-Ps through the processes mentioned above.

The intensity of the slow component (I_2) is thought to be equal to the ratio of the quantity of positrons which form t-Ps and then annihilated with a slow pick-off rate compared to that of the total of positrons. If there is a certain quantity of impurities in the system which can trap positrons, I_2 is decreased.

All these features of positron annihilation in condensed media may make it possible to obtain some useful information about the structure of the solids and active species trapped in them. Some experimental results on positron annihilation in irradiated organic solids have been already reported.[7-9]

For several years, we have been studying the positron annihilation phenomena in various monomer solids which can be polymerized by irradiation.[10] The polymerizing solids are one of the most interesting systems in which to apply the annihilation method to study the reaction mechanism, because a remarkable structural change occurs during polymerization. The present paper will report the results of the lifetime measurements of solid acrylamide and related compounds as a function of the irradiation dose.

Experimental

Acrylamide (AA) and propionamide (PA) were used for the experiment. AA was purified by sublimation, and the PA was recrystallized from methanol. A position source, about 15μ Ci of ^{22}NaCl enveloped in a thin nickel foil (5μ thick), was placed in the center of glass ampoule. The powdered monomer was introduced into the ampoule, which was then sealed off under a vacuum (1×10^{-4} mmHg). The internal radius of the ampoule was 12 mm, and the packing density of AA powder was about 0.6 g/cm^3. Under such conditions, only a negligible portion of positrons annihilated in the wall of the glass ampoule.

The lifetime of the positron in the solid monomers was measured before and after γ-ray irradiation with a ^{60}Co

1) J. Green and S. Lee,"Positronium Chemistry" Academic Press (1964).
2) "Positron Annihilation," ed. by A. T. Stewart and L. O. Roelling, Academic Press, New York (1967).
3) V. I. Goldanskii, *Atomic Energy Revies*, **6**, 3(1968).
4) R. K. Wilson, P. O. Johnson, and R. Stump, *Phys. Rev.*, **129**, 2091 (1963).
5) W. Brandt, *ibid.*, **120**, 1289 (1960).
6) A. M. Cooper, G. J. Laidlaw, and B. G. Hogg, *J. Chem. Phys.*, **46**, 2441 (1967).
7) G. Chandra, V. G. Kulkarni, R. G. Lagu, and B. V. Thosar, *Physics Lett.*, **16**, 40 (1965).
8) G. Fabri and E. Germagnole, *IL NUOVO CIM.*, **23**, 572 (1962).
9) J. H. Green and S. J. Tao, *Brit. J. Appl. Phy.*, **16**, 981 (1965).
10) Y. Tabata, Y. Ito, and K. Oshima, Paper presented at Symp. on Organic Solid State Chem., BNL., Mar. 1968.

source at 30°C. The dose rate was 2×10^5 R/hr. Since it took about 2 days to obtain a time spectrum with good statistics of the coincidence-counting rate, the samples were preserved at −78°C during the lifetime measurements. Therefore the post-polymerization of the irradiated solid monomers does not proceed during the lifetime measurement.

The lifetime was measured using a Weisberg-type time-to-amplitude converter[11] which had been constructed in our laboratory. Two $1\phi\times1$ in. Naton 136 scintillators coupled to Phillips 56 AVP photomultipliers were used as the detectors of γ-rays. The output pulse from the time-to-amlitude converter was analyzed by a 200-channel pulse-height analyzer. The resolution of the lifetime measurement, $W_{1/2}$, the full width at half maximum of the time spectrum of prompt γ-rays from a ^{60}Co source, was 0.7 nsec.

A FORTRAN IV program which can decompose a time spectrum into several components was made, and each time spectrum was analyzed with it by means of an electronic computor HITAC 5020, being thus decomposed into two components. The value of I_2 was calculated by the method of Green and Bell.[12] All attempts to decompose the spectra into three components were unsuccessful.

On the other hand, the polymerization of AA was followed by measuring the conversion of monomers to polymers. The polymers were isolated by dissolving the monomers in methanol. The irradiation of monomers was carried out under conditions similar to those in the case of the lifetime measurement, except that a positron source was not introduced with monomers in the ampoule. Furthermoer, the volume change of monomers during γ-ray irradiation was measured by dilatometry. For the experiment, the powdered monomer was pressed to make a tablet. The packing density was 0.85 g/cm^3, and the tablet was put into a dilatometer capsule.

Results and Disscussion

The powdered monomers were irradiated with a dose rate of 2×10^5 R/hr at 30°C. The annihilation rate λ_2, and the intensity, I_2, of the slow component as a function of the irradiation does are shown in Fig. 1. The kinetic curve of polymerization is shown in Fig. 2, together with the results of dilatometry. The kinetic curve is a typical S-shaped one composed of induction (0—1 Mrad), proparation (1—2 Mrad), and saturation (3 Mrad) periods.

The volume of the monomer decreases during polymerization, since the density is higher in the amorphous-polymer phase than in the crystalline monomer. The value of I_2 in the monomer crystal ($I_2=20.8\pm3.2\%$) is largest among several monomers examined by us.[10] A crystallographic study of the AA crystal[13] had shown that molecules form a layer through hydrogen bonding, and that the distance between adjacent layers is large. Therefore, we can expect there to be large free volumes between these layers. It would be expected that t-Ps can diffuse or jump into the large free volume in the AA crystals and be annihilated with a slow pick-off rate. On the other hand, there are several cases where t-Ps cannot encounter large free volumes in densely-packed crystals. In such cases, slow components can not be observed due to the rapid pick-off annihilation. Examples of the latter case are the monomer crystals of dimethylitaconate,[10] crystalline polyethylene,[14] and crystalline polytetrafluoroethylene.[15] In these solids, the

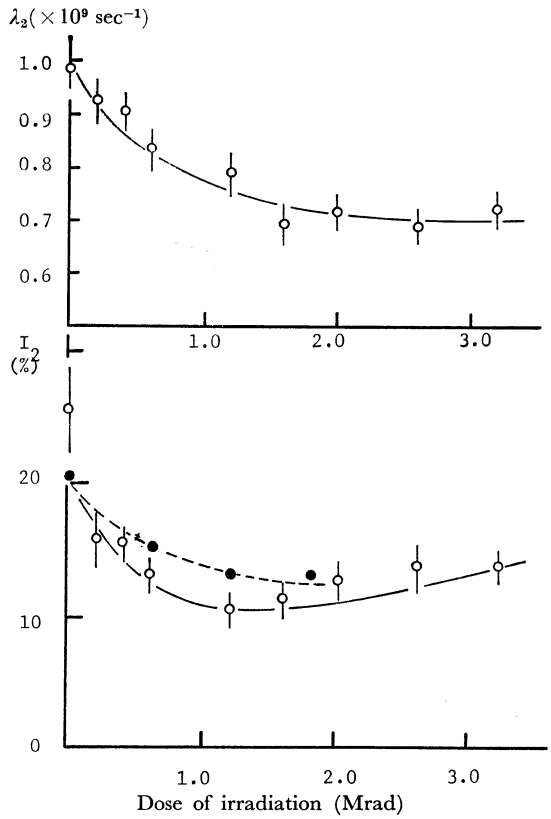

Fig. 1. λ_2 and I_2 in irradiated solid acrylamide as a function of irradiation dose. Irradiation was carried out at 30°C (-○-) and −78°C (--●--) with a dose rate of 2×10^5 R/hr. The bars at each point indicate the statistical average deviation of the counting rate.

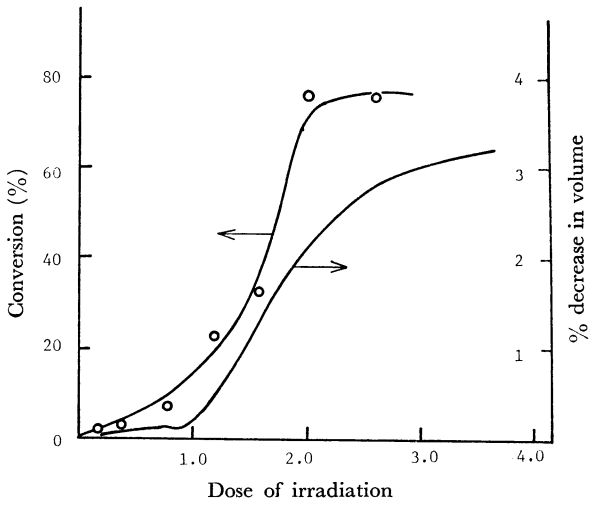

Fig. 2. Kinetic curve of polymerization in powdered AA(curve a) and result of dilatometry of AA tablet during polymerization. Dose rate: 2×10^5 R/hr. Temperature of irradiation: 30°C.

11) H. Weisberg, *Nucl. Instr. Method.*, **32**, 133 (1965).
12) R. E. Green and R. E. Bell, *Can. J. Phys.*, **35**, 398 (1957).
13) I. Nitta, I. Taguchi, and Y. Chatani, *Sen'iken Nenpo (Annual Report of Fiber Research)*, **12** 89 (1959).
14) S. J. Tao and J. H. Green, *Proc. Phys. Soc.*, **85**, 463 (1965).
15) W. Brandt and I. Spirn, *Phys. Rev.*, **142**, 231 (1966).

value of I_2 decreases with an increase in the crystallinity.

It must be noted that decreases in λ_2 and I_2 are observed in the induction period of polymerization. In the induction period, the conversion is still low, and the decrease in the overall volume of the solid is small, as is shown in Fig. 2. The decrease in λ_2 must be related mainly to the formation of a larger free volume, because any other annihilation processes of t-Ps, such as Ps compound formation or exchange collision, may only lead to an increase in λ_2.

It is known, as a result of the crystallographic study of the monomer, that the monomer molecules are closely aggregated in layers parallel to *bc* plane, and that there are 10 other double bonds within a distance of 5 Å from a double bond.[13] Therefore, the polymerization can be expected to proceed within a layer at the initial stage of polymerization, and the polymer phase produced can be expected to be separated from the monomer phase. Vacancies should then be produced around the polymer chains, and they make the free volumes larger by combining with original free volumes in the crystals. T-Ps can stay stable in such large free volumes and be annihilated at a lower pick-off rate. This may be the reason for the decrease in λ_2 during the induction period.

Figure 3 shows the results of the lifetime measurements of AA and PA irradiated at −78°C. Since PA is a saturated analogue of AA, it does not polymerize upon irradiation. Therefore, it is quite reasonable that λ_2 does not decrease on irradiation in the case of PA. On the other hand, λ_2 also decreases in AA irradiated at

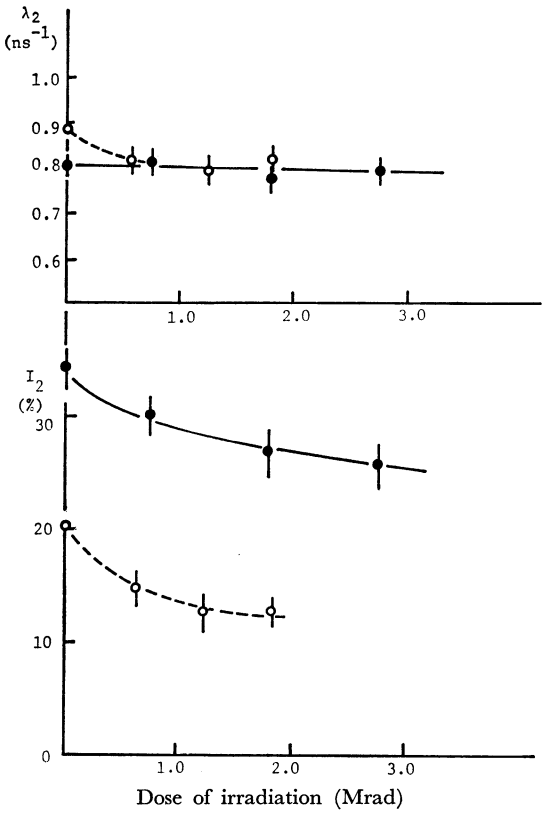

Fig. 3. λ_2 and I_2 in irradiated AA (--●--) and PA (-○-) as a function of irradiation dose. Irradiation was carried out at −78°C with a dose rate 2×10^5 R/hr.

−78°C. No polymer was detectable gravimetrically after irradiation at that temperature. However, there is an evidence that the oligomer is produced at low temperatures. For example, the ESR spectrum of AA irradiated at −196°C indicates the presence of the initiating radical species, but it changes to the spectrum of the propagating one when the temperature is raised above −94°C.[16] Therefore, the oligomer must be formed in AA irradiated at −78°C; in this case, larger free volumes are formed near the oligomer chains by a mechanism similar to that already explained.

It is interesting that λ_2 decreases to a small extent in the propagation period, in which the most remarkable change in the structure of the solid monomers must be taking place. This suggests that no free volume larger than that formed in the induction period is produced in the propagation period. As is shown in Fig. 1, the value of I_2 decreases in the induction period of the polymerization of AA. Since the decrease in I_2 was also observed in the irradiated PA (Fig. 3), the decrease in I_2 may not be directly correlated to the polymerization process. One possible explanation is that active species or impurities produced by γ-ray irradiation can capture positrons to form positron compound. Anothar explanation is that the quantity of free volumes which are responsible for the long-lifetime component in the AA solid monomer decreases gradually due to the polymerization in the crystal. Since I_2 decreases faster in a polymerizing AA solid at 30°C than in AA or PA irradiated at −78°C (Figs. 1 and 3), the decrease in the quantity of free volumes, together with the positron-compound formation, should occur in the polymerizing AA solid.

The value of I_2 is slightly increased in the later stage of polymerization (Fig. 1). This might be due to the effect of irradiation on the polymer produced. In order to determine whether or not this assumption is good, the lifetime of positrons in irradiated poly-AA was measured. Poly-AA was obtained by the radiation polymerization of the solid monomer. The procedure of sample preparation was the same as has already been described. Since the lifetime spectrum in poly-AA was complicated, we have not succeeded in decomposing it into several components. However, the lifetime spectrum did not practically change up to the irradiation dose of 2 Mrad, and at 3 Mrad the slow component apparently decreased. This result contradicts with the assumption made above, and the small increase in I_2 in the later stage of polymerization can not be attributed to the secondary effect of irradiation on the polymer produced.

Another possible explanation is that some active species which can capture positrons have disappeared due to annealing or recombination in the later stage of polymerization. This assumption seems to be supported by the following experimental results. The AA solid monomer, pre-irradiated to 2 Mrad at −78°C, was thermally treated, and the lifetime measurements were made. The variations in λ_2 and I_2 are indicated in Table 1, together with the conversion of post-polymerization. I_2 decreases with the irradiation dose at −78°C,

16) I. Nitta, S. Onishi, and T. Tanei, Paper presented at the 11th Annual Meeting of the Polymer Sci. (1962).

Table 1. Post-polymerization of acrylamide and lifetime measurement during the polymerization

	$\lambda_2 \times 10^9$ sec^{-1}	I_2 (%)	Conversion (%)
Before irradiation	0.883±.0033	20.8±3.2	—
After irradiation at −78°C(2Mrad)	0.861±0.039	13.1±1.9	trace
Kept for 2.5 hr at room temperature	0.796±0.047	14.9±2.3	4.2
Kept for 2.0 hr at 50°C	0.766±0.032	14.9±1.4	8.5
Further irradiation at−78°C(0.5 Mrad)	0.764±0.034	13.7±1.3	—

in agreement with the results presented in Fig. 3. However, it is slightly increased as post-polymerization proceeds. Therefore, a certain amount of active species which can capture positrons may have disappeared during the thermal treatment of the solid.

Conclusion

The lifetime spectrum has shown a remarkable change in the induction period of polymerization, and the decrease in λ_2 has been interpreted in terms of the formation of a larger free volume during polymerization. Such a free volume is also formed when oligomers are produced by the irradiation at low temperatures; the lifetime spectra have shown evidence of this.

I_2 also decreases in the induction period of polymerization, but this decrease may not be directly related to the polymerization process. Two possible explanations, that is, the accumulation of active species which capture positrons and the decrease in the number of free volumes, have been suggested. The former process may occur at least in the case of solid PA.

From these experiments, it has been clearly demonstrated that important information about the induction period can be obtained by the lifetime measurement of the positrons in solid monomers.[10] We expect that a detailed study of this kind may offer useful information concerning the mechanism of solid-state polymerization.

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